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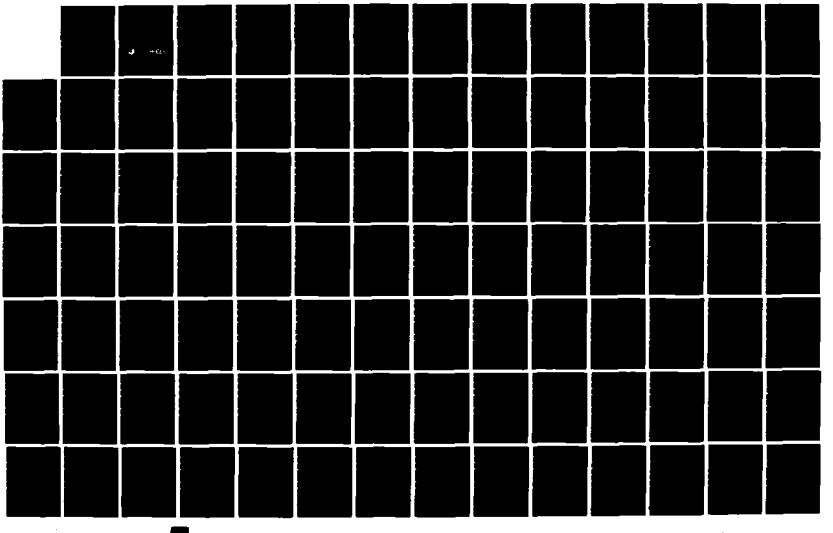

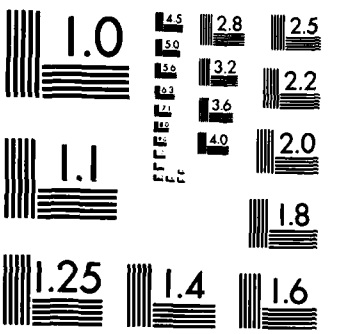

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Mass Transfer Coefficients and Henry's Constants for Packed–Tower Air Stripping of Volatile Organics: Measurements and Correlation

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Design of packed-tower air-stripping systems for the removal of volatile contaminants from groundwaters requires knowledge of the equilibrium constant relating air and water concentrations (Henry's constant, H), and the applicable mass transfer coefficient (K_La). The objectives of this research were: to evaluate the effects of temperature, ionic strength, and the mutual presence of other organics on the H-values of five volatile compounds of concern to the USAF; and to investigate the effects of temperature, packing size and type, liquid and air loadings, and the mutual presence of other organics on the K_La values of these same five compounds --tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, chloroform, and methylene chloride.

An innovative method for measuring Henry's constants was proposed and evaluated, termed Equilibrium Partitioning In Closed Systems (EPICS). This method relies upon measurement of the ratio of headspace concentrations from two equilibrated bottles containing equal solute

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BLOCK 19 (CONT.)
masses, but possessing differing liquid volumes. H-values for the five compounds were measured over temperatures ranging from 10° to 30°C using both EPICS and batch, diffused-bubble stripping techniques. Temperature regressions for H were derived. Comparison between methods suggests that EPICS is as precise as the batch-stripping technique, and is probably more accurate, being free of mass transfer limitations. In studies with organic mixtures up to 375 mg/l, no mutual effects on H were detected. Using KCl to adjust ionic strength (I), significant (> 10 percent) increases in activity were not evident until I > .26 M.

Liquid-phase diffusivity values were measured for the five study compounds at 20°C using a diaphragm diffusion cell. Due to solute mass losses through septa, data were imprecise. Thus, nothing in these results contraindicates the use of available diffusivity correlations.

Packed-tower air-stripping studies were performed using a pilot-scale facility of 44.5 cm (17.5-inch) ID by 2.44-meter (8-foot) packed height. Seven polypropylene packings were evaluated: 5/8-, 1-, 1 1/2-, and 2-inch rings; 1-inch saddles; 2-inch TriPacks®; and a structured packing. Temperature was controlled from 10° to 30°C. Liquid loading ranged from 0.6-1.38 m/min, and gas loading from 4.6-50 m/min.

Studies with all five solutes in mixture in the "mg/l" range, or in the presence of up to 500 mg/l methanol, showed no mutual effects on K_la values. The effect of temperature on K_la could be equally well-correlated through use of simple arithmetic, logarithmic, or viscosity-based expressions; however, due to the complexity of K_la dependence upon liquid and gas-phase parameters, these specific expressions are not expected to be applicable beyond the ranges of their derivation.

The Onda correlations for predicting K_la were evaluated. For all sizes of Pall rings, agreement with measured values was within 20 percent. For other packings, correlations appeared to systematically overestimate (e.g., 1-inch saddles) or underestimate (e.g., 2-inch TriPacks®) K_la values. Data for these could be generally fit within 30 percent by the Onda correlations. The systematic deviations noted for some packings suggests that additional geometric parameters need to be incorporated within the correlations.

BLOCK 18 (CONT.)
diffusivity, chlorinated, hydrocarbons, volatile organics, tetrachloroethylene, perchloroethylene, tetrachloroethene, 1,1,1-trichloroethane, trichloroethylene, trichloroethene, chloroform, trichloromethane, methylene chloride, dichloromethane, groundwater treatment, water treatment, water decontamination

BLOCK 11 (CONT.)
Henry's Constants For Packed-Tower Air Stripping of Volatile Organics: Measurements and Correlations

EXECUTIVE SUMMARY

Air stripping, using countercurrent, packed-tower systems, is an increasingly attractive technology for removal of volatile contaminants from groundwaters. Use of design and performance equations for such systems requires knowledge of the equilibrium constant relating air and water concentrations (Henry's constant, H), as well as the applicable mass transfer coefficient ($K_\ell a$). Both quantities are influenced by numerous system parameter values.

The main objectives of this research were: (1) to evaluate the effects of temperature, ionic strength, and the mutual presence of other organics on the H-values of five representative, volatile compounds presently of concern to the USAF; and (2) to investigate the effects of temperature, packing size and type, liquid and air loadings, and the mutual presence of other organics on the $K_\ell a$ values of these same five compounds -- tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, chloroform, and methylene chloride. Enroute to satisfying the above objectives, however, several additional accomplishments were realized, as described below.

An innovative method for measuring Henry's constants of volatile solutes in dilute aqueous systems was proposed and evaluated, termed Equilibrium Partitioning in Closed Systems (EPICS). This method relies upon measurement of the ratio of headspace concentrations from two equilibrated bottles containing equal solute masses, but possessing differing liquid volumes. Knowledge of the actual mass added to the two bottles is not required, nor is knowledge of the actual, resultant headspace concentrations; raw, surrogate measures such as gas-chromatographic peak heights suffice, so long as they are linearly related to actual concentration. Comparison of the EPICS procedure with a commonly used batch, diffused aeration method for measuring Henry's constant demonstrates that the EPICS procedure is at least as accurate, being free of mass transfer limitations which may affect the accuracy of other methods.

Henry's constant values were measured for the five selected volatile compounds over temperatures ranging from 10° to 30°C.

Temperature regressions were calculated and are reported for each compound. Experiments employing mixtures of the five solutes demonstrate no mutual effects on each others' Henry's constant at up to 375 mg/l total mixture concentration. Additionally, studies performed with the five solutes in the "mg/l" range, but in the presence of 200 mg/l phenol, showed no effect on Henry's constant. The effect of ionic strength on the activity coefficient of the aqueous solute was determined up to 1M KCl. "Salting-out" coefficients were thus derived. Significant (> 10 percent) increases in activity do not occur until the ionic strength of the system exceeds 0.26M (KCl).

Liquid-phase diffusivity values were measured for the five study compounds at 20°C using a horizontal diaphragm diffusion cell. Due to solute mass losses through septa, the data were somewhat imprecise. Therefore, comparison of values with diffusivities estimated with several available correlations was inconclusive. Nothing in the results obtained here contraindicates the use of "popular" correlations such as that of Wilke and Chang.

Packed-tower air-stripping studies were performed using a pilot-scale facility of 44.5 cm (17.5-inches) ID by 2.44-meter (8-foot) packed height. Seven polypropylene packings were evaluated: 5/8-, 1-, 1 1/2-, and 2-inch Pall rings; 1-inch Flexisaddles® 2-inch Tri-Packs®; and a structured packing (Flexipac)®. Temperatures were controlled and studied over the range from 10° to 30°C. Liquid loading ranged from 0.6-1.38 $m \cdot min^{-1}$; gas loading ranged from 4.6-50 $m \cdot min^{-1}$.

Studies performed with mixtures of all five solutes in the "mg/l" range showed no effect on the $K_\ell a$ value of each caused by the mutual presence of the others. The additional presence of substantial amounts of methanol used to predissolve the solutes caused no discernible effect on the $K_\ell a$ of each.

The effect of temperature on $K_\ell a$ could be equally well-correlated through use of simple arithmetic ($K_\ell a$ vs. T), logarithmic ($\ell n\ K_\ell a$ vs. T or $\ell n\ K_\ell a$ vs. 1/T) or viscosity-based ($K_\ell a$ vs. $T^{1/2} \mu_\ell^{-4/3}$) expressions; however, due to the complexity of $K_\ell a$

dependence upon liquid and gas-phase parameters, these specific expressions are not expected to be applicable beyond the ranges of their derivation.

The Onda correlations for predicting $K_\ell a$ were evaluated in these studies. For all sizes of Pall rings, agreement with measured values was within 20 percent, considered as good as could be expected. However, for other packings the $K_\ell a$ correlations sometimes considerably overestimated (i.e., 1-inch Flexisaddles)®, and sometimes underestimated (i.e., 2-inch Tri-Packs)® values. $K_\ell a$ data from Flexisaddles® and Tri-Packs® could be generally fit within $\pm$ 30 percent by the Onda correlations. Considering that the precision in measured $K_\ell a$ values is in the neighborhood of $\pm$ 10 percent, this level of agreement may suffice for many design purposes, if accompanied by an appropriate factor of safety.

Analysis of the $K_\ell a$ data and their deviations from correlation predictions demonstrate that no simple alteration of predicted $k_\ell a$ or $k_g a$ values (i.e., liquid and gas-phase resistances) by constant factors can consistently improve predictive ability. Observed performance differences between 1-inch Pall rings and 1-inch Flexisaddles® indicate that geometric parameters need to be incorporated into the correlations in order to properly modify them.

Pressure-drop measurements across the packed bed indicate inconsistent agreement between observed values and estimations provided by generalized correlations or manufacturer-supplied pressure-drop curves. Problems of scale-down are supposed.

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PREFACE

This report was prepared by the School of Civil and Environmental Engineering, Cornell University, Ithaca, NY 14853, under Contract F08635-82-K-0159 for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RDVW), Tyndall Air Force Base, Florida 32403-6001.

The report summarizes the pilot-scale determinations of mass transfer coefficients for seven packing materials and five chlorinated organic compounds in a packed-tower air stripper. Supporting laboratory determinations on aqueous diffusivities and Henry's Law constants are also presented. The work was performed between December 1981 and June 1984. The AFESC/RDVW Project Officer was Captain Randy L. Gross.

This report discusses the relative performance of seven commercially available, polypropylene packing materials. The report does not constitute an endorsement or rejection of any specific packing material for Air Force use, nor can it be used for advertising the product.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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LIST OF SYMBOLS[†]

A = diffusive path cross-sectional area in a diaphragm diffusion cell (cm^2)

A_x = cross-sectional area of a stripping tower (m^2)

A^* = total interfacial area in a bubble column (m^2)

A' = effective stagnant layer area for transfer in a diaphragm diffusion cell (cm^2)

B = diaphragm diffusion cell constant -- as used in this study

B_e = constant in Eyring's diffusivity equation

B_G = diaphragm diffusion cell constant -- as used by Gordon

B_H = diaphragm diffusion cell constant -- as used by Holmes

C_e = liquid effluent concentration of volatile solute ($mol \cdot m^{-3}$)

C_g = gas-phase solute concentration ($mol \cdot m^{-3}$)

C_g^* = theoretical gas-phase concentration which would be at equilibrium with a liquid-phase concentration of C_ℓ ($mol \cdot m^{-3}$)

C_ℓ = solute concentration in the liquid phase ($mol \cdot m^{-3}$)

C_ℓ^* = theoretical solute concentration in the liquid phase which would be at equilibrium with a gas-phase concentration of C_g or a partial pressure of P ($mol \cdot m^{-3}$)

C_z = solute concentration in a liquid sample taken at height z from a packed tower ($mol \cdot m^{-3}$)

D = diffusivity measured using diaphragm cell ($cm^2 \cdot s^{-1}$)

D_{AB} = diffusivity of solute A in solvent B ($m^2 \cdot s^{-1}$)

[†] Followed by usually used units; other comparable units may, at times, be used.

D_g = diffusivity of a solute in the gas phase ($m^2 \cdot s^{-1}$)

D_ℓ = diffusivity of a solute in the liquid phase ($m^2 \cdot s^{-1}$)

D_W = diffusivity of a solute in water ($m^2 \cdot s^{-1}$)

F = diffusing factor ($°K \cdot s^2 \cdot kg^{-1} \cdot m^{-1}$)

F_g = ratio of GC peak heights between two similarly prepared diffusion cell chambers (-)

F_s = stripping factor (-)

F_t = fraction of solute remaining at time t (-)

G = gas flow rate ($m^3 \cdot min^{-1}$)

G_m = gas mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$)

G_v = gas volumetric loading rate ($m \cdot min^{-1}$)

H = Henry's Constant for the solute ($m^3 \cdot atm \cdot mol^{-1}$)

H_c = dimensionless Henry's constant (-)

H^* = apparent Henry's constant = $H\gamma$ ($m^3 \cdot atm \cdot mol^{-1}$)

I = total ionic strength (-)

J = molecular mass transfer flux of the solute ($mol \cdot m^{-2} \cdot s^{-1}$)

K = factor in Scheibel diffusivity correlation

K_g = overall mass transfer coefficient based on gas-phase concentration units ($m \cdot s^{-1}$)

K_ℓ = overall mass transfer coefficient based on liquid-phase concentration units ($m \cdot s^{-1}$)

L = liquid flow rate ($m^3 \cdot min^{-1}$)

L_m = liquid mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$)

L_v = liquid volumetric loading rate ($m \cdot min^{-1}$)

M = quantity of solute present (mol)

M_f = final mass of solute remaining in system (relative units)

M_w = solvent molecular weight ($g \cdot mol^{-1}$)

N = solute transfer rate ($mol \cdot min^{-1}$)

P = partial pressure of solute in gas phase (atm)

P^* = theoretical partial pressure of solute which would be at equilibrium with a solute liquid concentration of C_ℓ (atm)

R = universal gas constant = 8.2056×10^{-5} ($m^3 \cdot atm \cdot mol^{-1} \cdot °K^{-1}$)
= 1.987 ($kcal \cdot mol^{-1} \cdot °K^{-1}$)

R_g = gas-phase resistance to mass transfer (s or min)

R_i = interfacial resistance to mass transfer (s or min)

R_ℓ = liquid-phase resistance to mass transfer (s or min)

R_t = total resistance to mass transfer (s or min)

S = integral value of dS differential interfacial elements within a packed tower (m^2)

T = temperature (°K or °C)

T_g = temperature at which the volumetric gas flow is referenced (°K)

U = superficial liquid velocity ($m \cdot s^{-1}$)

V = volume (m^3 or l)

V_a = molar volume of the solvent at its normal boiling point ($cm^3 \cdot mol^{-1}$)

V_b = molar volume of the solute at its normal boiling point ($cm^3 \cdot mol^{-1}$)

V_g = gas volume (m^3)

V_i = reactor liquid volume during the i^{th} time interval (m^3)

V_ℓ = liquid volume (m^3)

X = association factor for the solvent in the Wilke-Chang diffusivity correlation (-)

Z_t = total packed height of tower (m)

a = interfacial area per unit bulk volume of packing (m^{-1})

a_t = total, dry packing area per unit bulk volume of packing (m^{-1})

a_w = wetted interfacial area per unit bed volume (m^{-1})

d_p = nominal diameter of a unit of packing (m)

d_s = diameter of a sphere having the same surface area as a unit of packing (m)

g = acceleration due to gravity = 9.81 ($m \cdot s^{-2}$)

k = average mass transfer coefficient through each stagnant layer of a diaphragm diffuson cell ($cm \cdot s^{-1}$)

k_g = gas-phase mass transfer coefficient ($m \cdot s^{-1}$)

k_ℓ = liquid-phase mass transfer coefficient ($m \cdot s^{-1}$)

k_m = first-order constant for mass loss from a diffusion cell (h^{-1})

k_s = empirical "salting-out" coefficient (-)

ℓ = diffusive path length through the diaphragm of a diffusion cell (cm)

n = empirical constant for a particular packing (-)

p = GC peak height (relative units)

r_A = radius of a spherical solute (m)

s = fractional rate of surface renewal (s^{-1})

t = time (d, h, min, or s)

t_c = temperature (°C)

t^* = residence time of a fluid packet at the gas/liquid interface (s)

x_g = gas-phase boundary layer thickness (m)

x_ℓ = liquid-phase boundary layer thickness (m)

$\bar{y}$ = log-mean average mole fraction concentration in the gas (-)

z = height measured upward from the bottom of the tower packing (m)

ΔC_o = concentration difference between two solution chambers of a diffusion cell at time t = 0 ($mol \cdot m^{-3}$)

ΔC_t = concentration difference between two solution chambers of a diffusion cell at time t ($mol \cdot m^{-3}$)

ΔE = activation energy ($m^3 \cdot atm \cdot mol^{-1}$)

ΔH^o = standard enthalpy of dissolution ($kcal \cdot mol^{-1}$)

Δt_i = duration of the $i^{\underline{th}}$ interval (min)

α = empirical constant specific to a particular packing (-)

γ = activity coefficient (-)

δ = empirical constant specific to a particular packing (-)

ϵ = dry void fraction of a packed bed (-)

λ = correction factor; ratio of actual $k_\ell a$ to Onda-predicted $k_\ell a$ (-)

μ_g = gas viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)

μ_ℓ = liquid viscosity ($kg \cdot m^{-1} \cdot s^{-1}$)

μ_w = viscosity of water ($kg \cdot m^{-1} \cdot s^{-1}$)

ν = kinematic viscosity of liquid ($m^2 \cdot s^{-2}$)

ρ_g = gas density ($kg \cdot m^{-3}$)

ρ_ℓ = liquid density ($kg \cdot m^{-3}$)

σ = surface tension of liquid ($kg \cdot s^{-2}$)

σ_c = critical surface tension with respect to packing ($kg \cdot s^{-2}$)

ϕ = correction factor; ratio of actual $k_g a$ to Onda-predicted $k_g a$ (-)

% D = percentage difference of Onda-predicted $K_\ell a$ from measured $K_\ell a$

% R_g = percentage gas-phase resistance (of R_t)

SECTION I

INTRODUCTION

A. OBJECTIVES

The primary objectives of this research project were twofold:

1. To provide accurate Henry's constant data for five volatile organic solvents commonly found in contaminated groundwaters (tetrachloroethylene; 1,1,1-trichloroethane; trichloroethylene; chloroform; and methylene chloride). The effects of temperature and ionic strength on Henry's constants were investigated over ranges of 10-30°C and 0-1M (KCl), respectively.

2. To evaluate the accuracy of correlations for predicting overall mass transfer coefficients ($K_\ell a$ values) in packed-tower air stripping of dilute, volatile organics. The five compounds listed above were employed in packed-tower studies using a 44.5 cm ID (17.5-inch) by 3.05-meter (10-foot) stripping column with 2.44 meters (8 feet) of packing. Seven different packings were studied, each over wide ranges in gas and liquid loadings. For one packing, 2.54 cm (1-inch) polypropylene Pall rings, temperature was varied between 10°C and 30°C.

Several additional objectives were addressed through studies directed principally at the two primary objectives. For example, in the initial stage of Henry's constant investigation, the batch air-stripping method proposed by Mackay et al. (1979) was employed. The results at first seemed satisfactory, but later studies with dilute, aqueous mixtures of organics showed significant and unexpected effects on Henry's constants which suggested that the technique might suffer from failure to achieve gas/liquid equilibration. A novel technique is herein proposed -- Equilibrium Partitioning In Closed Systems (EPICS) -- which retains the advantages of the batch-stripping method, but does not suffer from equilibration limitations. Evaluation of the

EPICS method, and its comparison with the batch air-stripping method, comprised one important, additional objective of this research.

To expedite data acquisition, many investigators have measured Henry's constants and mass transfer coefficients using mixtures of volatile organics. Frequently, relatively large concentrations of methanol are also present, since methanol is commonly used as a solvent in the preparation of stock solutions of volatile, hydrophobic compounds. It is implicitly assumed that the volatility--and rate of volatilization--of the individual compounds are unaffected by the mutual presence of dilute concentrations of other organics. The assumption of independent volatilization is also made by design engineers when they employ data gathered from single-component studies in the design and analysis of air-stripping facilities for the treatment of groundwaters simultaneously contaminated by several organic pollutants. Hence, an additional objective of this research was to investigate the possible effect which dilute mixtures of volatile organics may have on the Henry's constants and $K_\ell a$ values of each.

The diffusivity of a solute in water plays an important role in governing the rate of volatilization. Empirical correlations (such as those of Onda) for $K_\ell a$ require diffusivity values as input data. However, virtually no experimental measurements of aqueous-phase diffusivities exist for the five compounds of interest to this study. Thus, empirical diffusivity correlations must be employed. An additional objective of this study was to measure aqueous-phase diffusivities of the five compounds and to evaluate the existing diffusivity correlations by comparing their respective predictions with experimental results. A diaphragm cell was employed for these measurements.

B. CONTEXT

Within the past several years the contamination of potable water supplies by synthetic organic chemicals has emerged as a major water quality issue in the United States. Several federal and state surveys have identified more than 300 hazardous organic chemicals in drinking

water (Symons, 1975). A recent study by Robeck and Love (1983) has estimated that approximately 15-20 percent of all groundwater supplies in the United States contain synthetic organic chemicals.

Among the most frequently detected compounds are volatile organic substances of low molecular weight such as trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, chloroform and methylene chloride (Roberts et al., 1982a). Evidence suggests that these compounds, even at very low concentrations, are potentially dangerous to human health. Experts allege that the extent of health damage from chronic exposure to volatile organic chemicals can range from skin disease to cancer, and may include dizziness, tremors and blindness (Council on Environmental Quality, 1981; Alexson, 1980). The Environmental Protection Agency (EPA) is currently assessing the inclusion of trichloroethylene, tetrachloroethylene and 1,1,1-trichloroethane in the National Revised Drinking Water Regulations.

Numerous cases hint at the geographic extent and severity of the groundwater contamination problem. Synthetic organic compounds have appeared in groundwater supplies in at least one community in each of 24 states. The majority of affected areas are located in the mid-Atlantic and New England states. Recent sampling has revealed significant organic contamination of wells in New York, New Jersey, Connecticut, Delaware, Rhode Island, Pennsylvania, Florida, Massachusetts and Michigan (Petura, 1981; Larson et al., 1983; Kim and Stone, 1980; Joyce, 1979; Althoff et al., 1981; Kelleher and Stover, 1981). Concentrations as high as 40 mg/l of 1,1,1-trichloroethane and trichloroethylene have been detected in some groundwater supplies (Dykssen and Hess, 1982).

Most incidences of groundwater contamination originate from improper disposal of organic chemicals at dumps or by land spreading, sanitary landfill leachate, accidental spills, and use of septic tank degreasing solvents (Symons et al., 1979; Gossett, 1983). Products used in water distribution systems are also sources of groundwater contamination. For example, tetrachloroethylene can be leached from vinyl-toluene-lined asbestos cement pipe (Larson et al., 1983).

Traditionally, granular activated carbon has been used to remove volatile organic compounds from groundwater. An innovative technique now receiving considerable attention is aeration (air stripping), in which water and air are brought into contact with each other to transfer volatile organic substances from water to air. The principle advantages of air stripping over adsorption are its simple design and operation, and its comparatively low cost. Both diffused aeration and packed-tower systems have been proposed and studied. However, compared to diffused aeration, packed-tower air stripping can achieve greater air-to-liquid ratios, and is therefore regarded as the more efficient aeration technique, on a performance basis, for removing volatile organics from water.

Although air-stripping technology has been well-developed in the chemical engineering literature (McCabe and Smith, 1976; Perry and Chilton, 1973), and has been used effectively to reduce the concentration of taste- and odor-producing compounds (McCarty et al., 1979), its application to the removal of synthetic organics from drinking water is much more recent. Because of their volatile nature, halogenated organics have been shown to be extremely amenable to air stripping.

A number of studies have successfully employed packed-tower air strippers for cleaning up contaminated groundwaters (Houel et al., 1979; Singley and Billelo, 1982; Mumford and Schnoor, 1982; Cummins and Westrick, 1983; Ball et al., 1984; and Riznychok et al., 1983). The city of South Brunswick, N.J. has employed an air-stripping tower to decontaminate aquifer waters containing tetrachloroethylene and 1,1,1-trichloroethane (Althoff et al., 1981). The U.S. Air Force, which has supported this research, is also using a packed tower to strip trichloroethylene from an aquifer in Michigan.

Procedures for designing packed-tower stripping systems require knowledge of Henry's constant and the applicable, overall mass transfer coefficient for the compound being stripped. Henry's constants for dilute solutions of volatile organic compounds can be estimated from compound solubility and vapor pressure data. However,

because accurate solubility data are often unavailable for these compounds, it is more prudent to measure Henry's constants.

Only a handful of studies concerning the measurement of Henry's constants exist in the literature (e.g., Munz and Roberts, 1982; Leighton and Calo, 1981; Kavanaugh and Trussell, 1980; Gossett, 1983). Variations of a method proposed by Mackay et al. (1979) have been commonly used. The technique employs a laboratory-scale, diffused-aeration column in which it is assumed that the exiting air bubbles achieve equilibrium with the mixed liquid contents of the column, allowing calculation of Henry's constant by monitoring the relative change in remaining liquid concentration with time. However, the time available for bubble equilibration is limited by the height of the column, which, in turn, is limited by the requirement for complete mixing of the liquid. Thus, the needs for equilibrium and complete mixing are at cross purposes.

The overall mass transfer coefficient ($K_{\ell}a$) varies with the specific organic compound, liquid and gas loadings, temperature, and with the packing material used. Recent design models suggest the use of empirical correlations to estimate the mass transfer coefficient (Kavanaugh and Trussell, 1980; Singley and Billelo, 1982). Numerous correlations are available in the chemical engineering literature (Perry and Chilton, 1973). However, these were developed for concentrated solutions and have not yet been extensively tested for use with dilute solutions of volatile organics.

The Onda correlations (Onda et al., 1968) seem to be the most promising for evaluating packed-tower stripping of volatile organics. This set of correlations, unlike many others, relies solely upon fundamental measurable properties of the stripping system. It can thus be easily adapted to a variety of systems. In limited testing, over a narrow range of liquid and gas loadings and for a few different packing types, it has proven to be a reliable method of predicting mass transfer coefficients for stripping of dilute organics (Cummins and Westrick, 1982; Roberts et al., 1982b; Singley and Billelo, 1982; Umphres et al., 1983; Ball et al., 1984). However, limitations in these previous studies must be stressed.

Many of the recent studies of volatile organic removal in packed-tower aeration have been in laboratory-scale facilities over a narrow range of operating conditions; low liquid and gas loadings and a limited variety of packings. A few pilot-scale studies have been reported (Umphres et al., 1983; Singley and Billelo, 1982; Ball et al., 1984) which cover a more realistic range of conditions. Nonetheless, information on the reliability of the empirical correlations for a variety of compounds, operating conditions, and packing types and sizes is still limited. Additional pilot-scale studies are needed to evaluate the existing correlations -- or to support suggestions for better correlations -- for predicting mass transfer coefficients of volatile organics over a range of fluid loadings and for a variety of packing types likely to be encountered in water treatment.

SECTION II

BACKGROUND

A. PERFORMANCE EQUATIONS FOR PACKED-TOWER AIR STRIPPING

The design principles for air stripping in packed towers have been extensively developed in the chemical engineering literature over the past 30 to 40 years (McCabe and Smith, 1976; Treybal, 1980). Chemical engineering applications generally involve design of systems to treat concentrated solutions. Most water treatment applications, however, involve concentrations of volatile organic contaminants usually less than 1 mg/l (Love and Eilers, 1982). The general design procedures developed in the chemical processing industry have recently been extended to the case of dilute solutions as typically encountered in water treatment applications (Kavanaugh and Trussell, 1980; Singley and Billelo, 1982; Cummins and Westrick, 1983).

For stripping of dilute solutions, development of the design equations can be simplified by the following assumptions (McCabe and Smith, 1976; Treybal, 1980):

- The amount of volatile compound in either phase is small with respect to the total volume of the phase; the volumes of the air and water streams do not change significantly during flow through the tower.
- A linear gas phase/solution phase equilibrium relationship exists for the compound being stripped; Henry's Law applies. That is,

$$P = HC_{\ell} \qquad (1)$$

where:

P = partial pressure of the solute in the gas phase (atm);
C_{ℓ} = solute concentration in the liquid phase ($mol \cdot m^{-3}$);
H = Henry's constant for the solute ($m^3 \cdot atm \cdot mol^{-1}$).

- The influent air does not contain any of the compound being stripped.

A brief development of the relevant performance equations is presented here. More detailed presentations are given in standard mass transfer texts (McCabe and Smith, 1976; Treybal, 1980).

A Schematic for a countercurrent packed column is shown in Figure 1. Contaminated water enters at the top of the tower and flows downward, counter-current to the air which flows up from the bottom. The contaminant is transferred from the water into the air. Define:

L = liquid flow rate ($m^3 \cdot min^{-1}$);
G = gas flow rate ($m^3 \cdot min^{-1}$);
$C_{\ell i}$ = solute concentration in the water ($mol \cdot m^{-3}$);
P_i = solute partial pressure in the air (atm);
$C^*_{\ell i}$ = theoretical solute concentration in the water at equilibrium with the partial pressure in the gas
= P_i/H, where $i = 1$ at the top of the tower and $i = 2$ at bottom of the tower;
Z_t = packed height of the tower (m);
A_x = cross-sectional area of the tower (m^2);
a = interfacial area per unit bulk volume of packing (m^{-1});
K_ℓ = overall mass transfer coefficient,

$$\left[\frac{\text{mol stripped}}{\text{min-m}^2\text{-(mol/m}^3\text{gradient)}}\right];$$

T_g = temperature at which the volumetric gas flow, G, is referenced (°K);
R = universal gas constant
= 8.2056×10^{-5} ($m^3 \cdot atm \cdot mol^{-1} \cdot °K^{-1}$).

From a material balance across the column, the moles of solute transferred out of the liquid must equal the moles of solute present in the exit gas:

$$L(C_{\ell 1} - C_{\ell 2}) = G(P_2 - P_1)/(RT_g) \qquad (2)$$

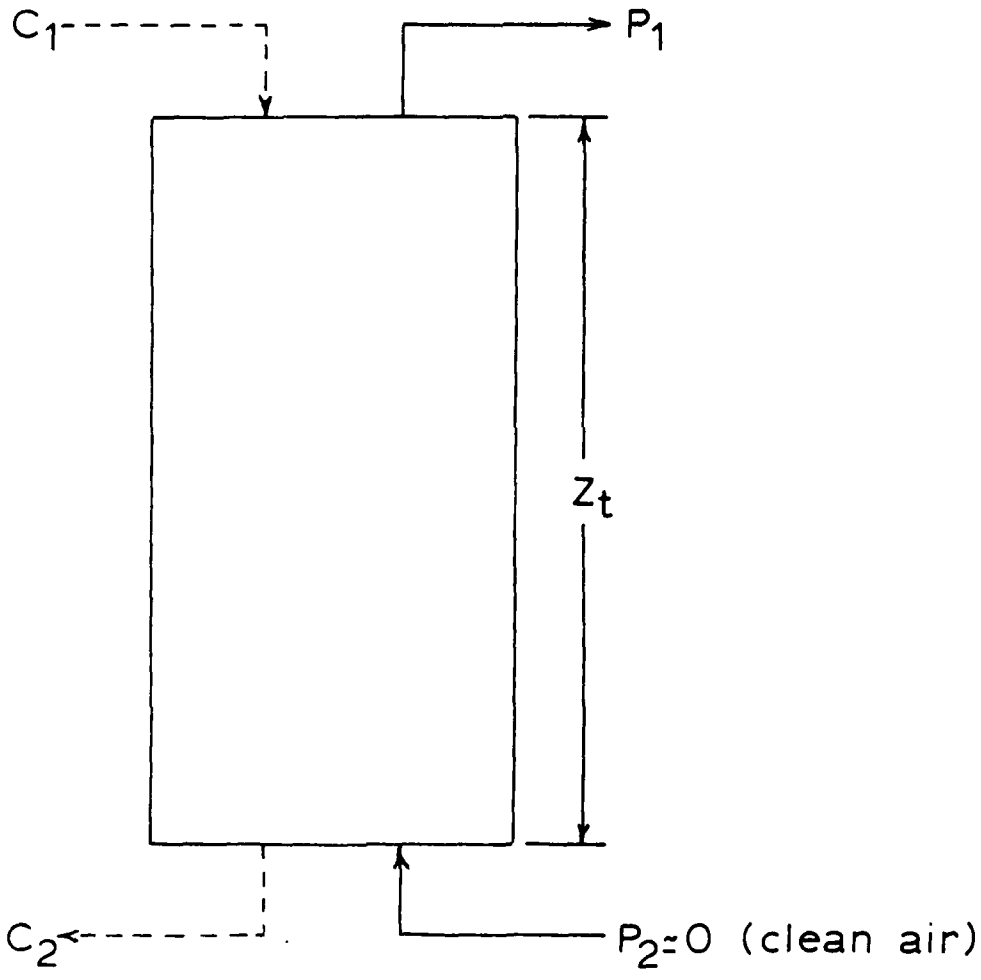

Figure 1. Schematic of Countercurrent Air-Stripping Tower.

If clean air enters the column, $P_2 = 0$, and

$$L(C_{\ell 1} - C_{\ell 2}) = GP_1/(RT_g) \tag{3}$$

The rate at which solute is transferred from the water to the air is proportional to the area available for transfer, and the difference between the bulk concentration of the solute and the expected equilibrium concentration. In general, the solute transfer rate would be a point quantity with respect to both space and time. However, if we consider only steady-state operation, then temporal distributions may be ignored. Thus, in differential form, the transfer rate, dN, through some differential surface element, dS, is expressed by:

$$dN = K_\ell (C_{\ell i} - C^*_{\ell i})dS \tag{4}$$

where:

dN = solute transfer rate through area dS ($mol \cdot min^{-1}$);

dS = differential interfacial element at some point within the packed bed (m^2).

If it s assumed that air and water flows are uniformly distributed within any cross section of the tower, then the solute transfer rate will vary only with height in the column. Thus, the differential area, dS, can be expressed in terms of a differential height variable, dZ, by noting that $dS = aA_x dZ$. Hence,

$$dN = K_\ell a(C_{\ell i} - C^*_{\ell i})A_x dZ \tag{5}$$

Integration over the height of the tower then gives the effective total removal rate of solute from the liquid:

$$L(C_{\ell 1} - C_{\ell 2}) = K_\ell a\overline{(C_{\ell i} - C^*_{\ell i})}_L A_x Z_t \tag{6}$$

The term $\overline{(C_{\ell i} - C^*_{\ell i})}_L$ represents the log-mean driving force for mass transfer across the tower. At any point in the column the driving force is proportional to the difference between the actual bulk concentration, $C_{\ell i}$, and the hypothetical equilibrium concentration, $C^*_{\ell i}$, which would exist if the bulk solution were at equilibrium with the local partial pressure in the air. Since the concentration in both phases varies throughout the tower, the

magnitude of this force changes. An effective average value is given by the log mean:

$$\overline{(C_{\ell i} - C^*_{\ell i})}_L = \frac{(C_{\ell 1} - C^*_{\ell 1}) - (C_{\ell 2} - C^*_{\ell 2})}{\ell n[(C_{\ell 1} - C^*_{\ell 1})/(C_{\ell 2} - C^*_{\ell 2})]} \qquad (7)$$

Returning to the overall mass balance, Equation (3), we know that $L(C_{\ell 1} - C_{\ell 2}) = GP_1/(RT_g)$, and according to Henry's Law, $C^*_{\ell 1} = P_1/H$ and $C^*_{\ell 2} = P_2/H = 0$ (if the incoming air is clean). Making these substitutions and rearranging Equation (6) yields:

$$\frac{C_{\ell 1}}{C_{\ell 2}} = \frac{\exp\left[\frac{Z_T A_x}{L}\left(1 - \frac{LRT_g}{GH}\right) K_\ell a\right] - \frac{LRT_g}{GH}}{1 - \frac{LRT_g}{GH}} \qquad (8)$$

Equation (8) allows prediction of the degree of removal achieved under specified operating conditions. It explicitly gives performance as a function of:

- column size, $Z_t A_x$;
- operating conditions, L and G;
- Henry's constant, H; and
- volumetric mass transfer coefficient, $K_\ell a$.

Hidden in these last two terms, H and $K_\ell a$, are a number of factors which implicitly affect performance. Henry's constant, H, is expected to be a function of the compound being stripped, the temperature, and the ionic strength of the solution. The volumetric mass transfer coefficient, $K_\ell a$, is even more complex; it depends on the compound, temperature, type and size of packing, and loading rates (i.e., superficial velocities) of each phase.

Discussions of gas/solution equilibria and mass transfer fundamentals are presented in this section. They provide the framework for a better understanding of the mechanisms through which Henry's constant and $K_\ell a$ are affected by the various physical and operational parameters. Quantifying these dependencies is another major objective of this research.

B. EQUILIBRIUM CONSIDERATIONS

1. Henry's Law

In 1803, William Henry observed that the volume of a gas that will dissolve in a given volume of water is independent of pressure (Gerrard, 1980). In other words, the mass of gas that will dissolve in a given volume of water is directly proportional to its pressure. The constant of proportionality between equilibrium gas partial pressure and liquid concentration is now known as "Henry's constant," and "Henry's Law" is expressed a number of ways. Two that are commonly used in the environmental literature are:

$$H = P/C_\ell \tag{9}$$

where:

H = Henry's constant of the solute ($m^3 \cdot atm \cdot mol^{-1}$);

P = partial pressure of the solute (atm);

C_ℓ = liquid phase solute concentration ($mol \cdot m^{-3}$).

and:

$$H_c = C_g/C_\ell \tag{10}$$

where:

H_c = Henry's constant in dimensionless units;

C_g = gas phase solute concentration ($mol \cdot m^{-3}$).

Henry's law is applicable only at low-solute concentrations. At higher concentrations, the equilibrium gas phase partial pressure of the solute is higher than Henry's law predicts. The concentration at which deviations from Henry's law begin to occur depends upon the chemicals in the system. In the water/ammonia system, which has been extensively studied, a plot of equilibrium partial pressure versus liquid concentration shows that deviations occur when the aqueous ammonia concentration is greater than 2780 mg/l (Kavanaugh and Trussell, 1980).

While such information is not available for the common pollutants in water, actual cases of groundwater contamination by hydrophobic pollutants usually involve such low concentrations that no deviations from Henry's law are expected. Experimental procedures for Henry's constant measurements, however, usually require much higher

concentrations to achieve precise results. If these measurements are to have any value, they must still be made within the range of concentrations which obey Henry's law. A number of researchers have measured Henry's constants, but few, if any, have offered proof that these measurements were made within the appropriate concentration range. Kavanaugh and Trussell (1980) state, "Research is urgently needed to obtain values of Henry's constants for low-contaminant concentrations typical of trace organic levels found in water supplies."

2. The Effect of Temperature on Henry's Constant

The temperature dependencies of equilibrium constants are generally modelled using a van't Hoff-type equation. For Henry's constant, such an equation would be:

$$\ln H = \Delta H^{o}/RT + K \qquad (11)$$

where:

ΔH^{o} = the standard enthalpy of reaction for the dissolution of the volatile compound ($kcal \cdot mol^{-1}$);

T = absolute temperature (°K);

K = an empirical constant;

R = the ideal gas constant ($1.987\ kcal \cdot mol^{-1} \cdot °K^{-1}$).

Reaction enthalpies tend to be constant over short temperature ranges, so a regression of $\ln H$ vs $1/T$ should be linear and can be used to derive an empirical temperature-dependence equation. Kavanaugh and Trussell (1980) and Leighton and Calo (1981) have published such equations for most of the compounds studied here. While both report high coefficients of determination for their linear regressions, indicating good precision, their results disagree significantly with each other for all compounds except chloroform.

3. The Effect of Ionic Strength on Henry's Constant

Nonzero ionic strength can cause a "salting-out" effect and an apparent increase in equilibrium constants for uncharged species in solution. Butler (1964) suggests modelling this phenomenon as a change in the activity coefficient (γ) of the uncharged species. Henry's law would then be written:

$$H = P/(\gamma C_\ell) \quad (12)$$

In solutions with no ionic strength, $\gamma = 1$, and Equation (9) is used. In solutions with appreciable ionic strength, the activity coefficient for an uncharged species is usually greater than one, and this causes an apparent increase in the compound's volatility. If the apparent Henry's constant, measured in a nonzero ionic strength solution is defined as H^*, then:

$$H^* = \gamma H \quad (13)$$

Butler's empirical equation for the ionic strength dependence of the activity coefficient is:

$$\log_{10}\gamma = k_s I \quad (14)$$

where:

I = the total ionic strength

k_s = an empirical "salting-out" coefficient

Combining Equations (13) and (14) yields:

$$\log_{10}H^* = k_s I + \log_{10}H \quad (15)$$

Equation (15) predicts a linear relationship between the log of effective Henry's constants and ionic strength. Although accurate k_s values are not available for the common hydrophobic pollutants, Butler states that for small uncharged molecules, the salting-out coefficients should be of the order of magnitude of 0.1, and independent of the salt species as long as they have unit charge. While this would not be true in complex natural systems, it would still be useful to measure k_s values for hydrophobic pollutants so that an approximate low range of ionic strength, where one could expect no significant effects on volatility, could be determined.

4. The Effect of Organic Mixtures on Henry's Constant

Changes in effective Henry's constants due to the presence of two or more dilute organic pollutants would have a significant impact on the treatment of groundwater pollution by air stripping, since most cases involve a complex mixture of contaminants. Groundwater contamination, however, rarely involves organic concentrations above a few parts per million. Therefore, one would not expect the contaminants to affect each other's volatility unless they were

chemically reactive. Dilling et al. (1975) report that most halogenated organics, including those studied here, are extremely inert, so such reactions are unlikely.

Most researchers determine the Henry's constants of compounds in a large mixture, relying on the unstated assumption that there are no interactions or effects on Henry's constants. This is done to save time. Another common research practice involves dissolving the slightly soluble organics in methanol prior to mixing them with water and measuring their aqueous Henry's constants. Again, it is assumed that the presence of methanol does not interfere with the Henry's constant determination.

Munz and Roberts (1982), in their discussion of a "tertiary" system (water, methanol, and one chlorinated hydrocarbon), claim to have shown from thermodynamics that the relatively small amounts of methanol used cannot affect the halogenated organic's Henry's constant. Munz and Roberts' proof rests on an equation derived by O'Connell and Prausnitz (1964), for a three-component, nonpolar system.* Munz and Roberts' "tertiary" system, however, was not only highly polar, but it also contained nine components: water, methanol, and a mixture of seven halogenated organics. In some of Munz and Roberts' experiments, there was actually a higher initial concentration of Freon 12 than there was of methanol. Munz and Roberts' experimental data show no significant effect upon the addition of methanol to the mixture, but the high concentrations of other chemicals present in the system make it difficult to draw positive conclusions from their results.

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* This equation is not germane to the study of dilute aqueous systems. It is designed to predict the behavior of "ideal" systems where there are only two particle, nonpolar interactions. O'Connell and Prausnitz found that it gave acceptable results for the prediction of the Henry's constant of hydrogen in a mixture ranging from pure heptane to pure toluene, but they found the behavior of a perfluoroheptane/iso-octane mixture "highly nonideal." The use of this equation for a water/methanol system is therefore suspect. O'Connell and Prausnitz stated that an equation similar to the one used by Munz and Roberts, but containing higher terms, would be needed to study polar solvents.

As there is no conclusive evidence justifying the simplification of experimental procedures by measuring Henry's constants in a mixture of organics, Henry's constant determinations for all compounds studied here were initially performed singly in distilled water, and then in mixtures.

C. DETERMINATION OF HENRY'S CONSTANT

1. Estimation by Vapor Pressure and Solubility

Theoretically, Henry's constants should be easily obtainable from vapor pressure and solubility data. If a three-phase closed system containing an organic layer, an aqueous layer, and a gas headspace is allowed to reach equilibrium, the aqueous-phase concentration would be the compound's solubility in water, and the gas-phase concentration would equal the vapor pressure of the pure compound.* Henry's constant, therefore, should equal the ratio of a compound's vapor pressure to its solubility in water, if the solubility is within the concentration range obeying Henry's law.

Mackay et al. proposed the estimation of Henry's constants from vapor pressure and solubility data in 1979. Their experimentally determined Henry's constants show their estimations to be quite accurate for the compounds studied (which are significantly less volatile than the compounds studied here). Unfortunately, available solubility data for the common groundwater contaminants are not accurate enough to allow estimation of Henry's constants for these compounds with better than "order-of-magnitude" confidence (Munz and Roberts, 1982). Further, for such information to be useful, accurate data would be needed over the ranges of temperatures and system compositions found in cases of groundwater contamination.

The most obvious method of measuring Henry's constant would be to allow a closed system containing air and a dilute aqueous solution of a chemical to reach equilibrium, and then simply measure

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* Strictly speaking, the gas-phase concentration should equal the vapor pressure measured over the water-saturated compound. For hydrophobic pollutants, however, this should be nearly equal to the vapor pressure of the pure compound.

the resulting liquid and gas concentrations. It is extremely difficult, however, to make accurate quantitative measurements of concentrations, particularly in the liquid phase. Attempts to prepare standard curves of volatile hydrophobic compounds in aqueous solutions rarely achieve standard deviations less than 20 percent (e.g., see the calibration curves of Munz and Roberts, 1982).

Since the common groundwater pollutants are all volatile liquids in their pure state, accurate mass addition for the preparation of standard solutions is difficult. Standard solutions could be prepared from saturated solutions, if accurate data on water solubilities were available. However, even if standard solutions were prepared, it would be extremely difficult to maintain their concentrations because of volatilization. These problems have led researchers to devise methods for measuring Henry's constants which do not require absolute concentration measurements.

2. Henry's Constant Determination by Batch Air Stripping

Batch air stripping for the determination of Henry's constants of hydrophobic pollutants was first proposed by Mackay et al. (1979). The technique is based upon a model of the transfer of a volatile chemical from a liquid into a gas–bubble stream. Mackay et al. list seven assumptions which must be true for the model to correctly measure Henry's constant. The two which are most difficult to ensure are:

- The concentration of organic in the gas bubbles must reach equilibrium with the surrounding liquid before leaving the liquid surface.
- The system must be completely mixed.

Under these conditions, the following equation can be used to predict the removal efficiency of a bubble column.

$$\ell n(C_\ell/C_\ell^o) = -(HG/VRT)t \qquad (16)$$

where:

C_ℓ = liquid phase concentration ($mol \cdot m^{-3}$);

C_ℓ^o = initial liquid concentration ($mol \cdot m^{-3}$);

H = Henry's constant ($m^3 \cdot atm \cdot mol^{-1}$);

R = universal gas constant ($m^3 \cdot atm \cdot mol^{-1} \cdot °K^{-1}$);

T = system temperature (°K);

G = gas flow rate ($m^3 \cdot h^{-1}$);

t = time (h);

V = column volume (m^3).

A plot of $\ell n\ C_\ell$ versus t gives a straight line with slope -(HG/VRT), and can be used to determine Henry's constant. It is not necessary to know the initial concentration, C_ℓ°, since it does not affect the slope of the line, nor is it necessary to prepare standard curves, since the conversion of raw concentration data to absolute concentrations would not affect the slope. Any relative measure of concentration, such as an absorbance or gas chromatograph peak can be used in the equation as C_ℓ, as long as there is a linear relation between it and absolute concentration.

a. Nonattainment of Equilibrium in Batch Air-Stripping Towers

If the bubbles do not reach equilibrium concentration, the right-hand side of Equation (16) must be multiplied by the fraction of equilibrium achieved, or an erroneously low Henry's constant will be measured. It should be pointed out that failure to correct for fraction of equilibrium achieved, or errors in its calculation, will not affect the linearity of the plot of Equation (16), only its slope. The data will appear to fit Equation (16), regardless of the degree of equilibrium, and this could lead to unfounded confidence in Henry's constant determinations made in stripping towers that do not actually achieve full equilibrium.

The fraction of equilibrium achieved is given by Mackay et al. as:

$$C_g/C_g^* = 1 - \exp(-K_\ell\ A^*RT/GH) \qquad (17)$$

where:

C_g = the bubble concentration achieved ($mol \cdot m^{-3}$);

C_g^* = the equilibrium concentration ($mol \cdot m^{-3}$);

K_ℓ = the overall liquid phase mass transfer coefficient ($m \cdot h^{-1}$);

A^* = the total interfacial area (m^2).

Inspection of Equation (17) reveals the factors influencing the attainment of equilibrium in batch air-stripping towers. When the dimensionless group ($K_\ell A^* RT/GH$) is greater than five, equilibrium is essentially complete, and Equation (16) can be used alone. Equilibrium is obviously favored by low Henry's constants, and is apparently favored by low gas flow rates (G). However, one cannot increase the degree of equilibrium simply by lowering the gas flow rate because the factors G, K_ℓ, and A^* are not independently variable, and it is extremely difficult to quantify changes in K_ℓ and A^*. If bubble size did not change with gas-flow rate, the ratio A/G^* would be constant, and changes in flow rate would have no effect on the fraction of equilibrium.

In practice, bubble size does decrease with decreasing gas flow, so that the overall effect is to increase the ratio A^*/G. This does not necessarily mean an increase in fraction of equilibrium, however, because K_ℓ also tends to decrease with decreasing bubble size (Munz and Roberts, 1982). It is, therefore, difficult to tell, even qualitatively, what effect changes in gas-flow rate have on the fraction of equilibrium achieved in a bubble column.

Mackay et al. suggest changing the liquid depth as a simple test to determine whether the system reaches equilibrium and Equation (16) can be used alone. If the Henry's constants measured at two different depths (using only Equation (16)) are identical, one can assume that equilibrium is achieved at both. If a higher Henry's constant is measured at the higher depth, then equilibrium was certainly not achieved at the lower depth.

The data of Mackay et al., however, show that this is not a simple test. They measured Henry's constants for benzene at 11 column depths, ranging from 0.9 to 38.5 cm. The data show a generally increasing trend, but no plateau. The difference between the Henry's constants measured at the maximum depth and the next

lower depth (14 cm) is greater than 20 percent. While this proves that equilibrium was not achieved at 14 cm, it does not prove that full equilibrium was reached at 38.5 cm.

Mackay's inability to conclusively prove that equilibrium was achieved for benzene in a 38.5 cm column is disconcerting because the most common groundwater pollutants have higher Henry's constants than benzene, and would therefore be less likely to reach equilibrium. One can ensure complete equilibrium only by using a taller tower, but this makes it more difficult to ensure complete mixing. As mentioned above, the theoretical derivations of Equations (16) and (17) require that the organic concentration is uniform throughout the column. It is difficult to predict what effect failure to achieve complete mixing would have on the measurement of Henry's constant.

Munz and Roberts (1982) suggest a method for determining $K_\ell A^*$, and the fraction of equilibrium achieved, and are confident that this will allow accurate measurement of Henry's constants in bubble columns that do not reach equilibrium. Munz and Roberts' technique requires the simultaneous absorption of oxygen into the bubble column liquid while stripping out the organics. Since the Henry's constant of oxygen is known, it is possible to measure the $K_\ell A^*$ of oxygen in the stripping tower.† If one then assumes that the $K_\ell A^*$ for the organic is proportional to that of oxygen, and that the proportionality is related to the ratio of their diffusivities raised to a power between 1/3 and 2/3, one can calculate a possible range for the $K_\ell A^*$ of the organic. Munz and Roberts take the average of this range and substitute it into Equation (17), allowing an iterative solution of Equations (16) and (17) for the Henry's constant of the organic.

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† A batch air-stripping tower that is far from reaching equilibrium is useful for measuring $K_\ell A^*$ (Matter-Muller et al., 1981). Since oxygen has a very high Henry's constant, it would remain far from equilibrium in the small stripping towers used to measure Henry's constants of volatile pollutants.

Aside from adding considerably to the complexity of the technique, both theoretically and experimentally, Munz and Roberts' data cast doubt on the accuracy of this method. The data show a dependence of Henry's constant on the $K_\ell A^*$ of oxygen, or the "turbulence" of the system. This also correlates with gas flow rate and average bubble size. Henry's constant however, is an equilibrium constant, and it cannot, as Munz and Roberts admit, be a function of any of these parameters.

To summarize the main difficulties in using batch air stripping to measure Henry's constants:

- It is difficult to prove that the condition of equilibrium has been achieved, even by changing the column depth.
- Methods for determining the fraction of equilibrium increase the theoretical complexity of the technique, and require an unguided estimation of the exponent of the diffusivity ratio of oxygen and the organic. These problems suggest that at the moment, only batch air-stripping towers that reach full equilibrium can be used to accurately measure Henry's constants.
- Taller stripping towers, designed to reach equilibrium for highly volatile compounds, might pose problems in complete mixing.

3. Equilibrium Partitioning in Closed Systems

To overcome the limitations of the batch air-stripping method for Henry's constant determination, a novel method was developed. Equilibrium Partitioning in Closed Systems (EPICS) is based on a comparison of mass balances in two similar systems. When a volatile chemical is added to a closed system containing both a liquid and a gas phase, a simple mass balance shows:

$$M = C_\ell V_\ell + C_g V_g \qquad (18)$$

where:

M = the mass added (mol);

C_ℓ = the concentration in the liquid ($mol \cdot m^{-3}$);

V_ℓ = the total liquid volume (m^3);

C_g = the concentration in the gas ($mol \cdot m^{-3}$);

V_g = the gas volume (m^3).

At equilibrium, the ratio of gas to liquid phase concentrations can be expressed as Henry's constant (Equation 10), and the mass balance can be rewritten to include Henry's constant:

$$M = C_g V_\ell / H_c + C_g V_g \tag{19}$$

If the same mass of organic is added to two systems (1) and (2) at the same temperature, but with different volumes, Equation (19) can be written for both and solved for Henry's constant:

$$H_c = \frac{(C_{g1}/C_{g2})V_{\ell 1} - V_{\ell 2}}{V_{g2} - (C_{g1}/C_{g2})V_{g1}} \tag{20}$$

Equation (20) expresses Henry's constant as a function of the ratio of concentrations in only one phase.* This allows measurement of Henry's constant without knowledge of exact concentrations or the preparation of standard curves. The ratio, C_{g1}/C_{g2}, can be replaced by a ratio of raw concentration data, such as gas chromatograph peak heights, provided only that there is a linear relationship between raw data and absolute concentration. It is not necessary to know the absolute mass added to each system. All that is required is that the masses are equal. This may be done, for example, by spiking each system with the same volume of organic-saturated water.

Plots of Henry's constant versus gas-phase concentration ratio (C_{g1}/C_{g2}) for various system volumes show that the technique has maximum sensitivity when one system has a low liquid volume and the

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* In this derivation, Henry's constant appears as a function of the gas-phase concentration ratio. An equation can easily be derived to express it as a function of the liquid concentration ratio instead.

other has a high liquid volume. If both systems had the same liquid volume (assuming they have the same total volume), they would be identical and could not be used to measure Henry's constant.

A plot for the closed systems used in these studies is shown in Figure 2. The total volume is 120 ml and the two liquid volumes are 10 ml and 100 ml. The technique may lose utility when the dimensionless Henry's constant (H_c) is greater than two or three, since the curve flattens out and the gas-phase concentration ratio becomes nearly constant with respect to Henry's constant. Fortunately, the most common groundwater pollutants have Henry's constants less than one throughout the temperature range of interest.

Successful measurement of Henry's constant by EPICS must meet three main conditions.

- The same mass of volatile compound is added to the two systems.
- Equilibrium between the gas and liquid phases is reached prior to measuring the gas-phase concentration ratio.
- Both systems are at the correct temperature.

The technique is fairly insensitive to errors in volume. An expansion of Equation (20) by partial derivatives shows that volume errors contribute an error to the variance of the Henry's constant measurement that is at least three orders of magnitude less important than errors in mass addition.

a. Determining Changes in Activity Coefficients by EPICS

The activity coefficient of an uncharged species in a salt solution could be measured, using high and low liquid volume systems as described above. A slight modification of the EPICS procedure, however, allows convenient measurement of changes in effective Henry's constants compared to those measured in distilled water.

If a closed system containing a volatile compound in distilled water is compared with one that also contains a third chemical, and the two systems have the same liquid volume, mass of

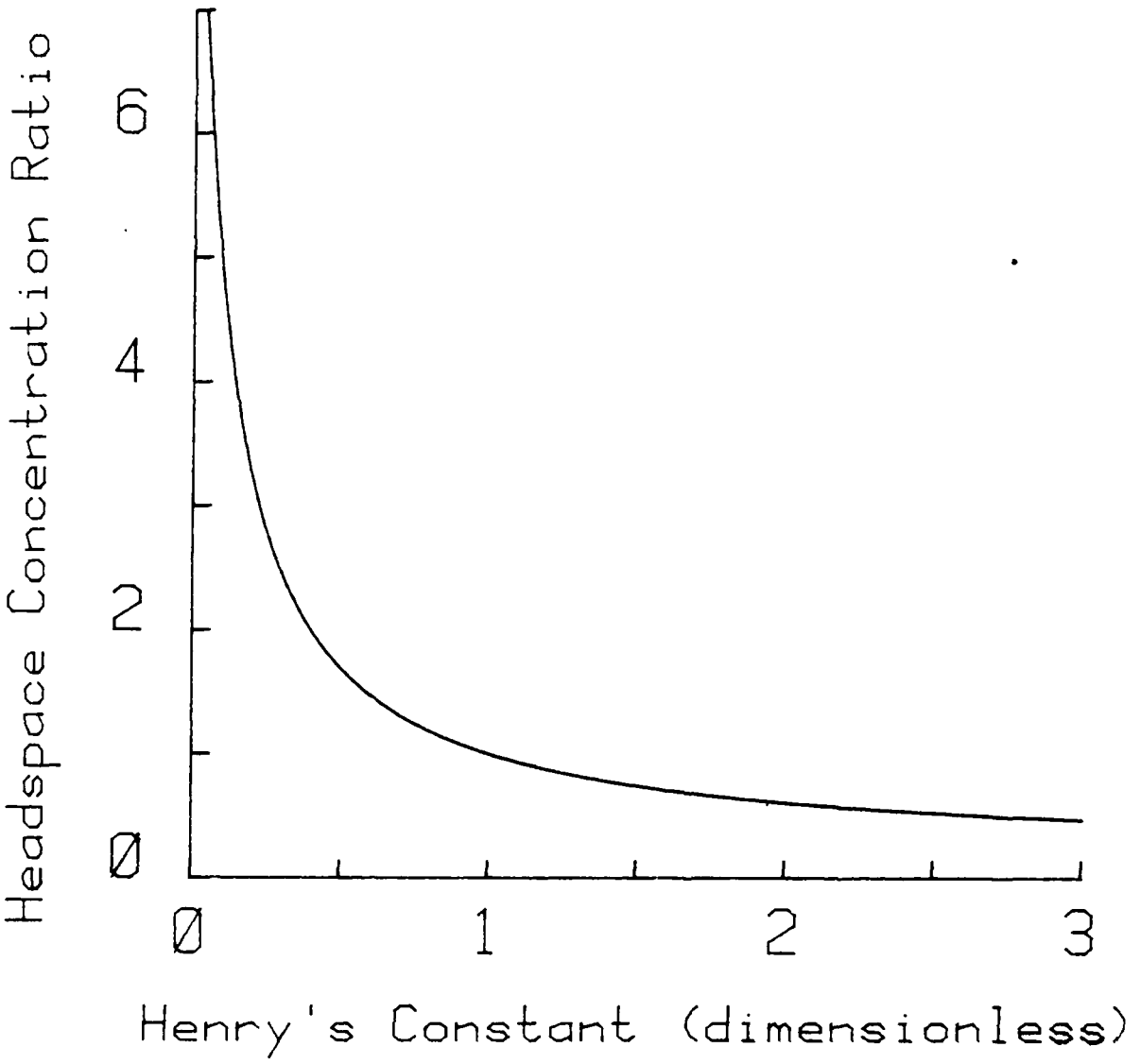

Figure 2. Headspace Concentration Ratio vs. Henry's Constant.

added volatile compound, and are at the same temperature, they will have the same equilibrium gas-phase concentration unless the effective Henry's constant changes. Equation (19) describes the equilibrium partitioning in the system containing only distilled water and the volatile compound. The equilibrium partitioning in the complex system is described by a similar equation which includes the activity coefficient (γ) of the volatile compound due to the presence of the third species:

$$M = C'_g V_\ell / \gamma H_c + C'_g V_g \qquad (21)$$

where:

C'_g = the equilibrium gas concentration of the volatile compound in the complex system ($mol \cdot m^{-3}$).

Equations (19) and (21) can now be equated and solved for the activity coefficient in the complex system:

$$\gamma = V_\ell / [C_g V_\ell / C'_g + V_g H_c (C_g / C'_g - 1)] \qquad (22)$$

where:

C_g = the equilibrium gas concentration in the reference system containing the volatile compound in distilled water only.

Inspection of Equation (22) shows that if the equilibrium gas phase concentrations are equal, the activity coefficient (γ) equals one, and there is no change in effective Henry's constant in the complex system. It can also be seen that this modification of the EPICS technique is most sensitive when the gas volume used is small. This modification is particularly useful because it allows the comparison of a whole range of complex solutions against a single reference system.

D. PRINCIPLES OF MASS TRANSFER

Mass transfer occurs at the boundary between a gas and a liquid. Several theoretical models have been developed to describe this transfer. The three most widely accepted models are the Lewis-Whitman two-film model (1924), the Higbie penetration model (1935), and the Danckwerts surface-renewal model (1951). The main differences among

these theoretical models lie in the physical interpretation of the transfer process.

1. Two-Film Theory

Lewis and Whitman (1924) developed a two-film model to describe mass transfer across a gas/liquid interface. This model hypothesizes that a thin, stagnant film or laminar boundary layer exists on each side of the interface. The bulk of each phase is assumed to be completely mixed. The solute migrates from the bulk of one phase to the interface, and then from the interface to the second phase. An underlying assumption of the two-film theory is that equilibrium conditions exist at the interface. This assumption of negligible interfacial resistance is valid under conditions of environmental significance (Raimondi and Toor, 1959; Chrostowski et al., 1982).

One conclusion derived from these assumptions is that the rate of mass transfer is controlled by molecular diffusion through each boundary layer. This is described by Fick's first law, which can be stated in one physical dimension as:

$$J = - D_{AB} \frac{\partial C}{\partial x} \qquad (23)$$

where:

J = the molecular mass transfer flux of the solute ($mol \cdot m^{-2} \cdot s^{-1}$);

D_{AB} = diffusion coefficient (diffusivity) of a solute A into solvent B ($m^2 \cdot s^{-1}$);

$\frac{\partial C}{\partial x}$ = concentration gradient ($mol \cdot m^{-4}$).

In Fick's formulation, J is really a point quantity, and concentration profiles can be obtained, in general, only by integration and solution of partial differential equations. However, if the boundary layer thicknesses are assumed constant (but not necessarily equal), as are the solute concentrations at the interface and at the outer edges of each thin film (where the solute concentrations in each phase are equal to their respective bulk concentrations), Equation (23) can then be written for the liquid phase and the gas phase, respectively, as follows:

$$J = \frac{D_\ell}{x_\ell}(C_\ell - C_{\ell i}) = k_\ell(C_\ell - C_{\ell i}) \quad (24)$$

and

$$J = \frac{D_g}{x_g}(C_{gi} - C_g) = k_g(C_{gi} - C_g) \quad (25)$$

where:

$k_{\ell,g} = \frac{D_{\ell,g}}{x_{\ell,g}}$ = phase-specific mass transfer coefficients ($m \cdot s^{-1}$)

$x_{\ell,g}$ = phase-specific boundary layer thicknesses (m);

C_ℓ = liquid-phase bulk solute concentration ($mol \cdot m^{-3}$);

$C_{\ell i}$ = liquid-phase solute concentration at the interface;

C_g = gas-phase bulk solute concentration ($mol \cdot m^{-3}$);

C_{gi} = gas-phase solute concentration at the interface;

D_ℓ = diffusivity of solute in liquid phase ($m^2 \cdot s^{-1}$);

D_g = diffusivity of solute in gas phase.

Essentially, the Lewis and Whitman model assumes steady-state diffusion to replace the gradients, $\partial C/\partial x$, by simple forms such as $(C_\ell - C_{\ell i})/x_\ell$. Concentrations at the interface cannot be measured, so overall mass transfer coefficients are defined, based on the difference between the bulk concentration in one phase and the concentration that would be in equilibrium with the bulk concentration in the other phase:

$$J = K_\ell(C_\ell - C_\ell^*) \quad (26)$$

and

$$J = K_g(C_g^* - C_g) \quad (27)$$

where:

K_ℓ = overall mass transfer coefficient based on liquid-phase concentration ($m \cdot s^{-1}$);

K_g = overall mass transfer coefficient based on gas-phase concentration ($m \cdot s^{-1}$);

C_ℓ^* = liquid-phase concentration that would be in equilibrium with the bulk gas concentration,

$= C_g/H_c$;

C_g^* = gas-phase concentration that would be in equilibrium with the bulk liquid concentration,

$= H_c C_\ell$.

Expanding Equation (26) to include the interfacial concentrations yields:

$$J = K_\ell[(C_\ell - C_{\ell i}) + (C_{\ell i} - C_\ell^*)] \quad (28)$$

Applying Henry's Law and substituting

$$C_{\ell i} = C_{gi}/H_c$$

and

$$C_\ell^* = C_g/H_c$$

into Equation (28) results in:

$$J = K_\ell[(C_\ell - C_{\ell i}) + (C_{gi} - C_g)/H_c] \quad (29)$$

In a situation where steady-state exists, with no accumulation at the interface, then the fluxes through both stagnant layers must be identical. Therefore,

$$J = K_\ell\left(\frac{J}{k_\ell} + \frac{J}{H_c k_g}\right) \quad (30)$$

This can be rearranged to yield:

$$\frac{1}{K_\ell} = \frac{1}{k_\ell} + \frac{1}{H_c k_g} \quad (31)$$

A similar manipulation of Equation (27) yields

$$\frac{1}{K_g} = \frac{H_c}{k_\ell} + \frac{1}{k_g} \quad (32)$$

Thus, overall mass transfer coefficients (K_ℓ, K_g) can be defined in terms of the individual film coefficients (k_ℓ, k_g) and Henry's constant.

The mass transfer coefficients can be viewed as conductivities and their reciprocals as resistances. Equations (31) and (32) are essentially the sum of two phase resistances in series to give an overall resistance. The total resistance, expressed either on a gas-phase ($1/K_g$) or liquid-phase ($1/K_\ell$) basis, depends on the mass transfer coefficients of the individual phases and the value of the Henry's constant for a particular solute. The total resistance to mass transfer may be written as:

$$R_t = R_\ell + R_g + R_i \quad (33)$$

where:

R_ℓ = the liquid-phase resistance;

R_g = the gas-phase resistance;

R_i = the interfacial resistance, which is assumed to be zero if the gas and liquid concentrations are in equilibrium.

It is important to note that additivity of resistances does not depend upon the two-resistance theory; indeed it is a fundamental principle. This concept is derived from assumptions common to all theories: (1) Henry's Law applies, (2) there is instantaneous equilibrium at the interface, and (3) the overall mass transfer rate is proportional to the difference between the bulk concentration in one phase and the concentration that would be in equilibrium with the bulk concentration in the other phase. Its validity may be demonstrated using alternative models, such as the penetration and surface-renewal theories.

Since the area across which diffusion occurs and the overall mass transfer coefficient cannot be determined independently, in most situations, the two terms are often combined and referred to as the volumetric mass transfer coefficient, $K_\ell a$ or $K_g a$. In such formulations the "a" portion of $K_\ell a$ or $K_g a$ may have two different meanings, depending upon the application. In most natural systems and in diffused-aeration applications, "a" refers to the effective interfacial area per unit liquid or gas volume. In packed-tower applications, however, it refers to the effective interfacial area per unit bed volume. In either case, "a" has units of reciprocal length.

2. The Penetration and Surface-Renewal Theories

A generally recognized flaw in the Lewis and Whitman two-resistance theory is the assumption of a steady-state rate of transfer and the subsequent prediction of a first-order dependence of the mass transfer coefficient on molecular diffusivity. Studies in surface aeration and air stripping have shown this dependence does not exist in highly turbulent systems (Tamir and Merchuk, 1978; Smith

et al., 1980, Dobbins, 1964). The penetration theory proposed by Higbie (1935) postulates that packets of the bulk solution are continuously transported to and from the laminar layer at the interface by turbulent eddies. All packets remain at the interface for the same brief period of time but, in contrast to the two-resistance theory, not long enough to attain steady-state. Instead, transient molecular diffusion governs mass transfer. Transient diffusion is described by Fick's second law:

$$\frac{\partial C}{\partial t} = D_{AB} \frac{\partial^2 C}{\partial t^2} \tag{34}$$

With the assumptions of uniform bulk concentrations and instantaneous equilibrium at the interface, the average liquid-phase mass transfer flux over the time a packet remains at the interface is:

$$J = 2\left(\frac{D_\ell}{\pi t^*}\right)^{0.5} (C_\ell - C_{\ell i}) \tag{35}$$

where:

t^* = time a packet remains at the interface.

Thus, the penetration theory defines the liquid-phase mass transfer coefficient to be:

$$k_\ell = 2\left[\frac{D_\ell}{\pi t^*}\right]^{0.5} \tag{36}$$

Danckwerts (1951) viewed the assumption of a constant exposure time (t^*) as unrealistic and amended Higbie's penetration theory to account for random replacement of the packets at the interface. In his surface-renewal theory, Danckwerts allowed a packet to be exposed to the surface for a time varying from zero to infinity. This theory adopts a probability function for the replacement of surface elements that is independent of the time an element has resided at the surface, resulting in the following mass transfer expression:

$$J = (D_\ell s)^{0.5}(C_\ell - C_{\ell i}) \tag{37}$$

where:

s = the fractional rate of surface renewal (s^{-1}).

Here, the liquid-phase mass transfer coefficient is defined:

$$k_\ell = (D_\ell s)^{0.5} \quad (38)$$

In contrast to the Lewis and Whitman two-resistance theory's linear dependence of the mass transfer coefficient on diffusivity, both Higbie's penetration theory and Danckwerts' important modification, the surface-renewal theory, predict a square-root dependence of k_ℓ on diffusivity.

3. General Remarks

All of the predictive equations for k_ℓ require the evaluation of certain parameters which are generally not well-defined and hard to measure. Regardless of the model used, the relationship between the mass transfer coefficient and the diffusivity is given by:

$$k_\ell = D_\ell^n / x_\ell \quad (39)$$

where:

n = 1 in the film theory;

n = 0.5 in the penetration and surface-renewal theories.

Experimental data suggest that the value of n lies between 0.5 and 1 (Tamir and Merchuk, 1978; Smith et al., 1980).

None of the foregoing theories is completely adequate in explaining gas transfer. However, the highly turbulent conditions found in packed towers lend reason to believe that the steady-state assumption of the two-film theory is somewhat simplistic. Therefore, mass transfer in packed towers is more likely governed by the surface-renewal theory.

4. Single-Phase Control of Mass Transfer

The overall mass transfer rate of a substance may depend on the liquid-phase or gas-phase resistance, or both, depending upon the relative magnitudes of the k_ℓ and $H_c k_g$ terms. For volatile organic compounds, the gas-phase resistance, $1/H_c k_g$, is often much smaller than the liquid-phase resistance, $1/k_\ell$ (Rathbun and Tai, 1981; Liss, 1977; Mackay et al., 1979; Matter-Muller et al., 1981; and Smith et al., 1980). In this case, the mass transfer is then said to be liquid-phase controlled, and Equation (31) reduces to:

$$1/K_\ell = 1/k_\ell \quad (40)$$

Based on exchange at the air-sea interface (Liss and Slater, 1974), it has been suggested that compounds with a Henry's constant (H_c) greater than 0.21 have 95 percent of the resistance to transfer in the liquid phase (Dilling, 1977; Mackay et al. 1979). According to this criterion, mass transfer for most compounds of concern in groundwater would be controlled by the liquid phase.

The hydrodynamics in a packed tower are different from those found in natural waters. Thus, the relative importance of the liquid- and gas-phase resistances differ. Roberts et al. (1982b) report evidence that for dimensionless Henry's constants (h_c) less than 1.0, more than 5 percent of the resistance to mass transfer, and in some cases more than 50 percent, is in the gas phase. As gas flow decreases relative to liquid flow, and as volatility decreases (i.e., H decreases), $k_g a$ has a greater influence on the overall mass transfer coefficient, $K_\ell a$ (Roberts et al., 1982b; Mumford and Schnoor, 1982; Umphres et al., 1983).

In modelling packed towers for removal of volatile organic compounds, it has been common practice to neglect the gas phase and assume that $K_\ell a = k_\ell a$ based on the criteria established for natural waters (Kavanaugh and Trussell, 1980; Mumford and Schnoor, 1982; Singley and Billelo, 1982; Umphres et al., 1983; Cummins and Westrick, 1982). If indeed $k_g a$ is significant, this approach can lead to overestimation of the overall transfer capacity. For packed-tower applications, it appears that a more realistic and conservative approach is to consider both resistances when estimating $K_\ell a$.

E. ESTIMATING $K_\ell a$

The volumetric mass transfer coefficient, $K_\ell a$, represents two quantities: K_ℓ, the overall mass transfer coefficient; and a, the effective area of contact between the two phases per unit of bed volume. In practice it is difficult to separate the two and they are often employed as the single quantity, $K_\ell a$.

Variables which influence K_ℓ in packed towers include the loading rate, viscosity, density and diffusivity of each phase; and the size and shape of the packing. Except for diffusivity, the same

variables control the interfacial area. The area is also affected by interfacial tension between the phases and wetting characteristics of the packing (McCabe and Smith, 1976).

Due to the complex nature of the overall mass transfer coefficient, $K_\ell a$, and its dependence on k_ℓ, k_g, and a, fundamental equations for estimating $K_\ell a$ are not available. Ideally, values of $K_\ell a$ for a specific system should be determined from pilot studies. However, in the absence of such data, a number of correlations in the literature can be used to estimate the value of $K_\ell a$. These correlations were empirically derived, although based on some simplified models of mass transfer.

Two types of models are cited: single-resistance models which assume $K_\ell = k_\ell$, and double-resistance models with expressions for both k_ℓ and k_g, which are then combined according to the two-resistance theory [Equation (31)]. Because of their empirical nature, caution should be used in applying these correlations outside of the range of conditions for which they were developed. Research is needed to test their reliability when applied to stripping of volatile organics. Three of the most widely used correlations are discussed below.

1. Sherwood and Holloway Correlation

In 1940, Sherwood and Holloway developed a single-resistance model for mass transfer. Assuming that gas-phase resistance was negligible, they estimated the overall volumetric mass transfer coefficient, $K_\ell a$, by the liquid-phase coefficient, $k_\ell a$:

$$\frac{k_\ell a}{D_\ell} = 10.764\ \alpha \left[\frac{0.3048\ L_m}{\mu_\ell}\right]^{1-n} \left[\frac{\mu_\ell}{\rho_\ell D_\ell}\right]^{0.5} \qquad (41)$$

where:

$k_\ell a$ = volumetric liquid mass transfer coefficient (s^{-1});

D_ℓ = solute liquid diffusivity ($m^2 \cdot s^{-1}$);

L_m = liquid mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$);

μ_ℓ = liquid viscosity ($kg \cdot m^{-1} \cdot s^{-1}$);

ρ_ℓ = liquid density ($kg \cdot m^{-3}$);

α,n = constants which are a function of packing type and size.

Equation (41) was developed from studies which examined the stripping of carbon dioxide, oxygen, and hydrogen from water with air in a tower packed with Raschig rings and Berl saddles. Liquid mass loading ranged from 0.34 to 44 $kg \cdot m^{-2} \cdot s^{-1}$ (250 to 32,000 $lb \cdot hr^{-1} \cdot ft^{-2}$) and gas mass loading was 0.04 to 1.8 $kg \cdot m^{-2} \cdot s^{-1}$ (36 to 1350 $lb \cdot hr^{-1} \cdot ft^{-2}$). Values of α and n were measured for several sizes of Berl saddles and Raschig rings.

2. Shulman Correlations

Use of Sherwood and Holloway's correlation is limited to systems where gas resistance is negligible and to packing types for which α and n are available. To overcome some of these limitations, Shulman et al. (1955b) developed a more fundamental approach. Separating the mass transfer coefficient from the interfacial area, they developed the following expressons for both liquid- and gas-phase mass transfer coefficients:

$$\frac{k_\ell d_s}{D_\ell} = 25.1 \left[\frac{d_s L_m}{\mu_\ell}\right]^{0.45} \left[\frac{\mu_\ell}{\rho_\ell D_\ell}\right]^{0.5} \tag{42}$$

$$\frac{\rho_g k_g (1-\bar{y})}{G_m} \left[\frac{\mu_g}{\rho_g D_g}\right]^{2/3} = 1.195 \left[\frac{d_s G_m}{\mu_g (1-\varepsilon)}\right]^{-0.36} \tag{43}$$

where:

d_s = diameter of a sphere having the same surface area as a unit of packing (m);

ε = dry void fraction of packed column;

D_g = diffusivity of the compound in the gas phase ($m^2 \cdot s^{-1}$);

G_m = gas mass loading rate ($kg \cdot m^{-2} \cdot s^{-1}$);

μ_g = gas viscosity ($kg \cdot m^{-1} \cdot s^{-1}$);

ρ_g = gas density ($kg \cdot m^{-3}$);

$\bar{y}$ = log-mean average mole fraction concentration in the gas.

The liquid-phase expression, Equation (42), was developed through reinterpretation of data reported by Sherwood and Holloway and

others. It is valid for liquid mass loadings from 0.65 to 9.7 $kg \cdot m^{-2} \cdot s^{-1}$ (500 to 7500 $lb \cdot ft^{-2} \cdot hr^{-1}$). Equation (43), the gas-phase expression, stems from data on vaporization of napthalene rings, at air-mass loadings ranging from 0.26 to 1.4 $kg \cdot m^{-2} \cdot s^{-1}$ (200 to 1000 $lb \cdot ft^{-2} \cdot hr^{-1}$) with volumetric gas-to-liquid ratios of 1 to 100.

An estimate of the interfacial area, a, is needed to obtain volumetric mass transfer coefficients from Equations (42) and (43). Recognizing that some of the liquid in the tower is caught in stagnant pools and is thus ineffective for transfer, Shulman defined the "effective" interfacial area, a_e. This value is smaller than the wetted area of the packing and is a function of gas and liquid loading and packing type. Effective areas for Berl saddles and Raschig rings are given in an extensive series of graphs in the original works (Shulman et al., 1955a and 1955b).

3. Onda Correlations

The most versatile and, thus, one of the most widely used set of mass transfer correlations was developed by Onda et al. in 1968. In contrast to Shulman, Onda assumed that the effective surface area equals the wetted surface area, a_w, and calculated k_ℓ and k_g by dividing measured values of $k_\ell a$ and $k_g a$ by a_w. The values obtained were then correlated with various dimensionless groups of operational variables:

$$k_\ell \left[\frac{\rho_\ell}{\mu_\ell g}\right]^{1/3} = 0.0051 \left[\frac{L_m}{a_w \mu_\ell}\right]^{2/3} \left[\frac{\mu_\ell}{\rho_\ell D_\ell}\right]^{-0.5} (a_t d_p)^{0.4} \quad (44)$$

$$\frac{k_g}{a_t D_g} = 5.23 \left[\frac{G_m}{a_t \mu_g}\right]^{0.7} \left[\frac{\mu_g}{\rho_g D_g}\right]^{1/3} (a_t d_p)^{-2.0} \quad (45)$$

where:

g = acceleration due to gravity = 9.81 $(m \cdot s^{-2})$;
a_w = wetted interfacial area per unit bed volume (m^{-1});
a_t = total dry packing area per unit bed volume (m^{-1});
d_p = nominal diameter of a piece of packing (m);

In Equation (45), the value 5.23 should be changed to 2.0 for packing smaller than 15 mm (Onda, 1968).

Onda defined the wetted area of packing, a_w, as a function of the liquid mass loading rate, physical properties of the liquid and the packing, the surface tension of the liquid, and the critical surface tension with respect to the packing:

$$\frac{a_w}{a_t} = 1 - \exp\left[-1.45\left(\frac{\sigma_c}{\sigma}\right)^{0.75} Re^{0.1}\, Fr^{-0.05}\, We^{0.2}\right] \qquad (46)$$

where:

σ_c = critical surface tension with respect to the packing material ($kg \cdot s^{-2}$);

σ = surface tension of the liquid ($kg \cdot s^{-2}$);

Re = Reynolds number $[L_m/(a_t \mu_\ell)]$;

Fr = Froude number $[L_m^2 a_t/(\rho_\ell^2 g)]$;

We = Weber number $[L_m^2/(\rho_\ell \sigma a_t)]$.

These expressions are based on gas absorption of hydrogen and carbon dioxide by water and organic liquids. The expression for k_ℓ is valid for liquid mass loadings of 1 to 15 $kg \cdot m^{-2} \cdot s^{-1}$ (700 to 11,000 $lb \cdot ft^{-2} \cdot hr^{-1}$). Onda (1968) reported an error of $\pm$ 25 percent for Raschig rings, Berl saddles, spheres and rods. The k_g expression correlates to within $\pm$ 30 percent for the same packings at gas mass loadings from 0.02 to 1.7 $kg \cdot m^{-2} \cdot s^{-1}$ (15 to 1250 $lb \cdot ft^{-2} \cdot hr^{-1}$).

4. Correlations for Interfacial Area

In addition to Onda's expression for a_w there are several other expressions for interfacial area -- wetted and effective. Three of the more generally adaptable are presented here. Using data from columns packed with Raschig rings, Berl saddles, and spheres, Yoshida and Koyanagi (1962) published the following correlation:

$$\frac{a_w}{a_t} = 0.079\left[L_m\left(\frac{\sigma}{20}\right)^{3q}\right]^{1/3} \qquad (47)$$

where:

$q = -0.74\, d_p^{-0.70}$

Mada et al. (1964) define the interfacial area as

$$a = \frac{0.34}{d_p} Fr^{-1/2} We^{2/3} \quad (48)$$

The most recent correlation for interfacial area was presented in a summary of tower correlations written by Hughmark in 1980. He presented the following general equation for interfacial area:

$$a = \left(\frac{\delta g^{1/2}}{a_t^{\alpha + 0.5}} \right) \frac{U^{\alpha}}{\nu^{\alpha + 1}} \quad (49)$$

where:

g = acceleration due to gravity ($cm \cdot s^{-2}$);
a = interfacial area per unit volume (cm^{-1});
U = superficial liquid velocity ($cm \cdot s^{-1}$);
ν = kinematic viscosity ($cm^2 \cdot s^{-2}$).
α, δ = packing-specific constants, extensively tabulated in the original article.

5. Previous Evaluations of Mass Transfer Correlations

Recently, several investigators have evaluated the different correlations for use in design of packed towers for stripping volatile organics. These studies indicate that the two-resistance correlations of Shulman and Onda are overall much better at predicting values of $K_\ell a$ than the single-resistance correlation of Sherwood and Holloway.

Using the Sherwood and Holloway expression, Roberts et al. (1982b) reported agreement within 20 percent between measured and predicted $K_\ell a$ values for highly volatile compounds and for less-volatile compounds at high gas flow rates. However, Sherwood and Holloway's correlation consistently overestimated $K_\ell a$ for low gas flow rates and slightly volatile compounds.

Umphres et al. (1983), in pilot-plant studies of trihalomethane removal, reported similar results; good agreement for highly volatile compounds but poor agreement (20 to 90 percent difference) for less volatile bromoform ($H_c = 0.2$). The Sherwood and Holloway expression was employed by Ball et al. (1984) to evaluate pilot plant performance for air stripping of five volatile organic compounds.

Here again, the data and predicted values agreed except for bromoform, the least volatile of the compounds studied, where predicted and measured values differed by a factor of two.

The lack of fit for compounds of intermediate volatility (H_c < 0.3) and for low gas flows suggests that the assumption of negligible gas resistance may be invalid and that a two-resistance model is needed. This result is consistent with two-resistance theory, which predicts that gas resistance becomes more important as Henry's constant decreases.

Shulman and Onda both predict overall mass transfer coefficients based on gas- and liquid-phase resistances. Both sets of correlations show $K_\ell a$ to decrease as gas flow decreases, in agreement with observed behavior (Riojas et al., 1983).

The literature contains very few references to use of the Shulman correlations for volatile organic removal. One laboratory-scale evaluation, however, (Roberts et al., 1982b) indicated that this set of correlations does not agree as closely as do the Onda correlations with measured values of $K_\ell a$. Roberts et al. reported that $K_\ell a$ values estimated from Shulman's correlations were 30 percent less than measured values. The effective area may be the source of this deviation.

The Onda correlations seem to be the most promising for evaluating packed-tower stripping of volatile organics. The ability to calculate a_w in addition to mass transfer coefficients allows the model to be adapted to a variety of systems. Also, recent investigations show Onda to be fairly reliable for predicting $K_\ell a$ values in packed towers treating dilute systems of volatile organics. Cummins and Westrick (1982) reported excellent agreement (standard deviation of 17.8 percent) between measured $K_\ell a$ values and $K_\ell a$ values calculated using Equations (44), (45) and (46). The Onda correlations fit data collected by Roberts et al. (1982b) within $\pm$ 20 percent.

There is some evidence that the correlations are less reliable when applied to conditions outside the range used in developing the expressions (Cummins and Westrick, 1982). At low gas flow rates the Onda correlations consistently overestimated actual

values of $K_\ell a$ (Roberts et al., 1982b). The same trend was noticed for slightly volatile compounds, where Onda tended to predict higher $K_\ell a$ values than measured values. Both of these conditions correspond to an increased influence of $k_g a$, which suggests that the Onda correlations may underestimate the effect of gas-phase resistance.

Most of the studies discussed have been performed in laboratory-scale facilities, over a limited range of operating conditions. Umphres et al. (1983) and Singley and Billelo (1982) conducted the most comprehensive studies; however, both studies used the Sherwood and Holloway model for comparison.

Umphres et al. measured $K_\ell a$ values in a 30 cm (12-inch) diameter column packed with 2.54 cm (1.0-inch) Intalox saddles. Liquid loadings ranged from 0.08 to 1.3 $m \cdot min^{-1}$ (2 to 32 $gal \cdot min^{-1} \cdot ft^{-2}$) at gas to liquid ratios (vol/vol) of 40, 90, and 100. Singley and Billelo conducted studies using a 38 cm (15-inch) column packed with 2.54 cm (1.0-inch) saddles. The maximum liquid loading was 1.7 $m \cdot min^{-1}$ (42 $gal \cdot min^{-1} \cdot ft^{-2}$), and maximum gas loading was 40 $m \cdot min^{-1}$, to give gas-to-liquid ratios of from 7 to 30.

Before the correlations can be effectively and confidently used in design, more comprehensive investigations are needed to prove their reliability over a wide range of operating conditions and for different packing types and sizes.

F. INFLUENCE OF MIXTURES ON $K_\ell a$

Most air-stripping investigations are conducted without verifying the assumption that organic mixtures have no effect on the volatility or transfer rate of each volatile component of the mixture. Quite frequently, researchers try to expedite experimentation by dissolving mixtures of these relatively insoluble volatile organics in methanol before adding them to water for stripping studies. It is implicitly assumed that the volatile organics do not interact, and the addition of methanol has no influence on $K_\ell a$. However, the mass transfer coefficient and Henry's constant may both be affected by the presence of additional organics, either by surface activity effects, or through solute-solute interaction.

1. Postulated Effects of Surface-Active Substances on $K_\ell a$

Many organic substances tend to concentrate at the gas-liquid interface and can interfere with mass transfer. Although the mechanisms by which this occurs are not completely understood, most researchers agree that surface-active substances tend to reduce the rate of mass transfer in aeration systems (Davies and Rideal, 1963; Adamson, 1967; Mancy and Okun, 1965; Plevan and Quinn, 1966; Goodridge and Robb, 1965; Matter-Muller et al., 1981; Burnett and Himmelblau, 1970; Onda et al., 1968; Liss and Martinelli, 1978; Smith et al., 1980).

A surface-active substance (surfactant) can alter the rate of mass transfer by influencing k_ℓ, the liquid film coefficient, or the interfacial area, a. Effects on k_ℓ may include alteration of hydrodynamic activity and addition of an interfacial resistance, both through accumulation of surfactant at the interface. The interfacial area is affected by changes in surface tension.

a. Hydrodynamic/Boundary Layer Mechanism

Advocates of the two-film theory might explain the reduction in k_ℓ by an increase in the thickness of the stagnant boundary layer, x_ℓ. Since k_ℓ is inversely proportional to x_ℓ, the rate of mass transfer would be reduced. The surface-renewal theory also predicts a decrease in k_ℓ by surface-active agents; alteration of hydrodynamic flow conditions may result, since surfactants suppress or eliminate interfacial turbulence that normally occurs at the gas/liquid interface (Lee et al., 1980).

Several theoretical investigations involving the hydrodynamic effect of surface active agents on mass transfer between a single drop and a continuous phase have been reported. Garner and Hale (1953) and Garner and Skelland (1956) have explained the decline in mass transfer as resulting from the suppression of internal circulation inside drops. Lee et al. (1980) and Ternovskaya and Belopolski (cited by Vrentas, 1963) have observed a similar effect during oxygen absorption in a stirred cell and wetted-wall column.

Studies on the suppression of interfacial motion in packed columns due to surfactants are scarce. Hikita et al. (cited by

Onda et al., 1968) noticed a decrease in $k_{\ell}a$ when a commercial surfactant was added to a packed column during gas absorption of carbon dioxide into water. They attributed this effect to a reduction in liquid mixing at the junction between packing pieces. Unfortunately, Hikita's studies were limited to relatively low-turbulence regimes (Reynold's numbers less than 20), and may not apply to more turbulent conditions.

Davies et al. (1964) have shown that the reduction in mass transfer due to the addition of surfactants varies markedly with the degree of turbulence. At short contact times, the surface active substance has no chance to establish an adsorbed layer at the interface. Surface eddies are not dampened when there is rapid surface renewal. Thus, for highly turbulent systems (e.g., packed columns operated at high liquid flow rates), it seems unlikely that added surfactants influence the hydrodynamic flow patterns (Sherwood et al., 1975).

b. Interfacial Resistance to Diffusivity

In addition to reducing interfacial motion or increasing the thickness of the stagnant boundry layer, surface-active substances can also contribute an intrinsic interfacial resistance to mass transfer. Goodridge and Robb (1965) have speculated that this resistance arises when a surfactant alters the properties of the interface. These authors have indicated that the interfacial resistance effect, also referred to as "the diffusive barrier effect," and the hydrodynamic effect operate simultaneously.

Thompson (1970) was able to eliminate surface motion by applying fine mesh screens to the liquid surface. He still found a considerable decrease in the mass transfer rate in the presence of surfactants. Emmert and Pigford (1954) restricted surface rippling in a wetted-wall column and discovered that the mass transfer rate was lowered by 25 percent upon adding a surfactant. Caskey and Barlage (1972) studied the effects of surfactants on gas absorption in laminar jets and observed that surface films offered appreciable resistance to mass transfer. Similar conclusions about nonhydrodynamic interfacial

resistance have been reached by other investigators (Goodridge and Bricknell, 1962; Vrentas, 1963; and Mackay, 1982).

The transport of solute molecules from the liquid phase through the interface to the gas phase involves a series of resistances or barriers to diffusion. Recall that the two-film theory assumes that equilibrium exists at the interface and that the interfacial resistance, R_i, is negligible [see Equation (33)]. However, in the presence of surfactants, R_i can no longer be ignored. As a result, the total resistance to transfer, R_t, increases and K_ℓ decreases because $K_\ell = 1/R_t$.

Mackay (1982) has developed a model which predicts the behavior of diffusing solutes in the presence of surface-active films. The model estimates the relative contributions for retarding k_g and k_ℓ due to a combined diffusive resistance and hydrodynamic effect. According to Mackay, the hydrodynamic effect influences k_ℓ to a greater extent than k_g. Liss and Martinelli (1978) have determined that when transferring oxygen and low solubility halogenated hydrocarbons, the interfacial film will merely add to the existing liquid-phase resistance. Mackay (1982) has also indicated that the interfacial resistance should be low for these substances since they are probably as soluble in the interfacial region as in the bulk.

c. Effects on Interfacial Area

The importance of the interfacial area of contact between a gas and a liquid suggests that any substance which affects the wetted area on a solid, such as a packing piece, should influence the rate of mass transfer in a packed tower. Surface-active substances act to decrease the interfacial free energy by lowering the liquid surface tension, and cause the interfacial area to increase (Matter-Muller et al., 1981).

The relationship between surface tension and the interfacial area for transfer is quantitatively described by Onda et al. (1968) [see Equation (46)]. The interfacial area, a, which is considered to be equivalent to the wetted area, a_w, is influenced by--among other things--the ratio of the critical surface tension of

the packing to the liquid surface tension (i.e., σ_c/σ). The critical surface tension refers to the surface tension at which a liquid will wet a solid material. Wetting is the spontaneous spreading of a liquid to a monomolecular layer on a solid surface (Adamson, 1967). Typical values for plastic packing material are: 33 dynes/cm for polyethylene, 28.5 dynes/cm for polypropylene (Fowkes, 1964), and 18 dynes/cm for Teflon (Zisman, 1964). If the other variables in Equation (46) remain constant, Onda et al. predict that as the liquid surface tension decreases, the ratio σ_c/σ approaches unity, and the wetted area will increase.

d. Summary of Surfactant Effects

The overall mass transfer coefficient, $K_\ell a$, may increase, decrease or remain the same in the presence of surface active agents depending on the degree to which k_ℓ or a is modified.

Surfactants decrease k_ℓ by:

- suppressing interfacial turbulence or by increasing the stagnant boundary layer thickness;
- contributing an interfacial resistance or barrier to diffusivity.

Surfactants increase a by:

- lowering surface tension, thereby permitting the packed surface to wet more effectively.

2. Solute-Solute Interactions

In addition to surface activity effects, the rate of mass transfer may be influenced by interactions among the solutes. The only way in which methanol and the five volatile organics could affect each other's rate of transfer is if they are chemically reactive. Dilling et al. (1975) and Rathbun and Tai (1981) have indicated that most chlorinated organics are extremely difficult to degrade. Grayson (1981) and Dilling et al., have summarized the hydrolysis of halogenated organics, including those studied here. According to Dilling et al., breakdown of these compounds in water does not occur until the temperature is well above ambient (i.e., > 100°C).

Therefore, one would not expect hydrolytic reactivity at the temperatures employed in air-stripping experiments.

Mackay and Yeun (1983) have investigated the possibility of interaction among organic solutes volatilizing simultaneously. These researchers found that the volatilization rates of compounds in a mixture of carbon tetrachloride, benzene, toluene, and nine other organics at concentrations in the 1 mg/l range did not differ significantly from rates observed in individual compound studies. It was concluded that these solutes volatilize independently, and no interaction occurred at these low concentration levels.

Rathbun and Tai (1981) have studied the effect of simultaneous volatilization of chloroform, methylene chloride, benzene, and toluene at concentrations of about 1 mg/l. A statistical analysis of variance considering single component studies as one class and four component studies as another class showed no significant difference at the 1 percent level. These investigators concluded that any interaction among the solutes had a negligible effect on the liquid film coefficient.

Using a bubble air-stripping column, Munz and Roberts (1982) have demonstrated that methanol, at concentrations up to 120 µg/l, has virtually no effect on the rate of transfer of chloroform, trichloroethylene, carbon tetrachloride, and tetrachloroethylene. They concluded that methanol behaves more like water than an n-alcohol. Dilling et al. (1975) have also reported that the evaporation rates of chlorinated organics are the same in the presence or absence of methanol. Therefore, it follows that, although the volatile organic compounds are physically dissolved in the methanol, they probably do not react chemically with the methanol.

G. THE EFFECT OF TEMPERATURE ON $K_\ell a$

Temperature does not appear as an explicit parameter in any of the various mass transfer correlations. Nonetheless, $K_\ell a$ is a function of temperature via effects on fluid properties, Henry's constant, and diffusivities of the compound being stripped. The amounts of change in temperature-sensitive parameters pertinent to air stripping are

TABLE 1. EFFECTS OF TEMPERATURE ON SYSTEM PARAMETERS.

Parameter	Value at 10°C	Value at 30°C	% Change
Gas Viscosity (10^{-5} kg•m^{-1}•s^{-1})	1.76	1.86	+ 5.7
Gas Density (kg•m^{-3})	1.248	1.165	- 6.7
Gas-Phase Diffusivity)[a] (example: TCE) (10^{-6} m^2•s^{-1})	7.22	8.21	+ 13.7
Liquid Viscosity (10^{-3} kg•m^{-1}•s^{-1})	1.307	0.798	- 38.9
Liquid Density (kg•m^{-3})	999.7	995.7	- 0.4
Liquid-Phase Diffusivity[b] (example: TCE) (10^{-5} cm^2•s^{-1})	0.700	1.23	+ 75.7
Surface Tension of Water (kg•s^{-2})	0.0742	0.0712	- 4.0
Henry's Constant[c] (example: TCE) (dimensionless)	0.173	0.440	+154

[a] Calculated, using Hirschfelder correlation (Hirschfelder et al., 1954).

[b] Calculated, using Wilke-Chang correlation (Wilke and Chang, 1955).

[c] Gossett (1983).

presented in Table 1. There is substantial change in many of the variables, especially Henry's constant, liquid viscosity, and liquid-phase diffusivity. Although the precise effect on $K_\ell a$ cannot be predicted without invoking one of the available sets of mass transfer correlations, the direction of the change in the mass transfer coefficient with an increase in temperature is apparent; the decrease in Henry's constant and liquid-phase diffusivity all tend to increase $K_\ell a$.

The quantitative effect of temperature on $K_\ell a$ could conceivably--if not conveniently-- be ascertained by substituting the various temperature-corrected parameter values into one of the empirical correlations for $K_\ell a$. Given the complexity of the relationships involved, it is apparent that the sensitivity of $K_\ell a$ to temperature will depend upon (among other things) the percent gas-phase resistance, which, in turn, depends upon loading rates, the volatility of the compound, and the packing used. For example, a temperature-sensitive parameter such as Henry's constant will only affect $K_\ell a$ if there is appreciable gas-phase resistance. Otherwise, $K_\ell a \simeq k_\ell a$, and the gas-resistance term containing H_c will not exert significant impact. Thus, while information such as contained in Table 1 tempts one to conclude that the largest effects of temperature upon $K_\ell a$ may be due to variation in H_c with temperature, it is not reasonable to conclude this without going through detailed calculations tailored to the specific system conditions under investigation. No quantitative generalizations are valid.

1. Experimentally Observed Temperature Effects

Temperature plays a significant role in mass transfer; however, little experimental data are available concerning the effect of temperature on air-stripping operations. Additionally, the reliabiity of empirical expressions such as Onda's correlations over a range of temperatures has not been established. It is surprising that so few systematic temperature studies have been performed, since mass transfer facilities used in water and wastewater treatment must operate effectively over a range of temperatures both between different facilities and within one facility over the course of a year.

The effect of temperature has been qualitatively, if not also quantitatively, described by few investigators. Mackay and Leinonen (1975) performed an evaporation study of the half-lives of low-solubility compounds and reported that "The mass transfer coefficients and aqueous solubilities are relatively temperature-insensitive." (Note: A half-life is the time required under specified experimental conditions for the concentration of a volatile compound to drop to half its initial value. Therefore, it is related to the mass transfer coefficient for that compound under the study conditions.) They concluded that half-lives are insensitive to temperature and referred to their data for benzene at 10°C and 25°C for support. Many authors have used this stated conclusion to neglect the effect of temperature, when in fact the data obtained by Mackay and Leinonen did reflect a 5 percent decrease in the liquid-phase mass transfer coefficient, a 4.5 percent increase in the half-life, and a 51.5 percent decrease in Henry's constant for benzene over the 15°C temperature range of their study. Given that benzene is not one of the most volatile compounds ($H_c \approx 0.22$ at 25°C based on Mackay and Leinonen data) and that Mackay and Leinonen report only two data points, their interpretations of the results and the results themselves should be used with caution until verified by further study.

In a similar study, Dilling (1977) investigated the evaporation rates of low-molecular-weight chlorohydrocarbons. Although most evaporation rates were determined at 25°C, he did observe an increase in the half-lives obtained from one experiment executed at 1-2°C, an increase which he attributed primarily to the change in Henry's constant. However, he did note more of an effect than could be accounted for solely by the change in Henry's constant, suggesting that the difference between the observed and predicted half-lives could be due to his assumption of temperature-independent liquid- and gas-phase mass transfer coefficients.

In a rare systematic temperature study, Kozinski and King (1966) reported a substantial effect of temperature on liquid-phase mass transfer coefficients in a stirred vessel; an effect which they modelled using an exponential relationship ($\ell n\, K_\ell a \propto T$).

The effect of temperature has also been noted in packed-tower experiments, although it has rarely been investigated systematically. The magnitude of the temperature effect depends on the characteristics of the compound being stripped, the effect being much larger for the mass transfer coefficient in the liquid phase than in the gas phase (Treybal, 1980). The greater dependence of the liquid-phase mass transfer coefficient is also implied by the information presented previously in Table 1, although changes in Henry's constant will multiply the temperature-induced change in gas resistance over that of the changes in the gas-phase mass transfer coefficient alone. Singley and Billelo (1982) stated that the temperature dependence they observed in the air stripping of volatile organics was indicated by the variation in H_c. Treybal suggested the magnitude of the temperature effect determined experimentally can be used to indicate which resistance controls mass transfer.

Kavanaugh and Trussell (1980) reported that both H_c and $K_\ell a$ decrease with decreasing temperature, making stripping more difficult. Tower depth and/or diameter would have to be increased to obtain the same removal efficiency at a lower temperature. Expanding on these conclusions in a later report (Kavanaugh and Trussell, 1981), they reported a 50 percent decrease in H_c and a 10 percent decrease in the mass transfer coefficient for chloroform as temperature dropped from 20 to 10°C. Goers and Hubbs (1982) also noted a decrease in the effectiveness of both packed tower and cascade air stripping in removing chloroform and bromodichloromethane over the temperature range of 23 to 18°C. In an air-stripping study of sludge containing chloroform, Lumb (1977) observed a temperature-induced acceleration in the rate of stripping.

Despite the observed effect of temperature on performance, none of the studies above attempted to model explicitly the effect of temperature on mass transfer coefficients. One of the few efforts to specifically correlate mass transfer coefficients with temperature was Sherwood and Holloway's (1940) classic study of the desorption of carbon dioxide, oxygen, and hydrogen using a packed tower. These three compounds have negligible gas resistance, so the results of

their study are limited to the effect of temperature on the liquid-phase mass transfer coefficient. Sherwood and Holloway obtained a log-linear relationship between $K_\ell a$ and temperature from 5-40°C. The results for CO_2 and O_2 were almost identical, which was expected from the closeness of their liquid-phase diffusivities. The mass transfer coefficients for H_2 were significantly higher than for CO_2 and O_2; however, the effect of temperature on all three compounds could be modelled as follows:

$$K_\ell a \ (= k_\ell a) \propto \exp(0.023\ t_c) \tag{50}$$

where:

t_c = temperature (°C).

Sherwood and Holloway concluded that the temperature effect was independent of the liquid loading rate and solute gas.

In a similar study, Vivian and King (1964) determined the liquid-phase resistance of five sparingly soluble gases (helium, hydrogen, oxygen, carbon dioxide, and propylene). Combining their results with those of Sherwood and Holloway, they obtained

$$K_\ell a \ (= k_\ell a) \propto \exp(0.020\ t_c). \tag{51}$$

In the only other systematic study of the effect of temperature, Gossett (1983) modelled the mass transfer coefficient of trichloroethylene from 10 to 30°C using an Arrhenius-type dependency:

$$K_\ell a = \exp[8.518 - (2515/T)] \tag{52}$$

where:

T = temperature (°K).

A correlation of this form was equally effective in modelling the temperature dependence of $K_\ell a$ as the exponential model employed by Sherwood and Holloway and Vivian and King.

2. Temperature Effects Predicted by Onda's Correlations

Consider the complexity of the two-resistance model for mass transfer given by Equation (31). It becomes apparent that, since a_w k_ℓ, k_g, and H_c all are temperature-dependent quantities, there can be no simple, explicit temperature regression for $K_\ell a$ that would be

generally applicable to a variety of stripping systems with different packings and loadings. Only in cases where gas-phase resistance is negligible (and $K_\ell \simeq k_\ell$) would explicit models of the type presented above be potentially useful for general application. Otherwise, the best approach would seem to be to evaluate the effect of temperature on each parameter in the Onda correlations and apply the full, two-resistance model. As pointed out earlier, however, this approach has not been systematically evaluated.

If gas resistance is ignored, the Onda correlation for k_ℓ can be used to obtain a simple, explicit temperature regression for K_ℓ. Neglecting any temperature dependence in a_w, and assuming that operating conditions other than temperature remain constant, the Onda correlations predict:

$$K_\ell a \propto D_\ell^{1/2} \mu_\ell^{-5/6} \tag{53}$$

Diffusivities are not well-established for many compounds, but the product of diffusivity and viscosity divided by temperature ($D_\ell \mu_\ell / T$) is at least approximately constant for any one compound (Reid and Sherwood, 1977). Therefore, Equation (53) can be further reduced to:

$$K_\ell a \propto T^{1/2} \mu_\ell^{-4/3} \tag{54}$$

If valid, Equation (54) could be useful in estimating the effect of a temperature change on mass transfer. To compare the different models developed in experimentally determined temperature correlations to the reduced Onda equation, viscosity can be expressed in terms of temperature using the Andrade correlation (Reid and Sherwood, 1977):

$$\mu_\ell \propto \exp(M^*/T) \tag{55}$$

where:

M^* = constant.

Equation (54) can then be equivalently expressed as:

$$\ln K_\ell a = V - (X/T) + 0.5 \ln(T) \tag{56}$$

where V and X are constants. In dilute aqueous stripping applications, V would depend upon gas and liquid loadings, packing, and solute, whereas X would truly be constant.

None of the relationships developed here, either determined from the Onda correlations or from experimental observation, should be used without experimental verification of their validity under intended conditions.

H. THE EFFECT OF LOADING RATES ON $K_\ell a$

Liquid- and gas-loading rates are among the more important design and operating variables affecting stripping tower performance. In addition to direct effects [see Equation (8)], fluid loadings also influence performance via effects on $K_\ell a$. The two-resistance correlations of Onda or Shulman predict that $K_\ell a$ will increase as either liquid or gas loading increases. The magnitude of this dependence is a function of the relative importance of the gas- or liquid-phase resistance in determining the total mass transfer resistance.

Results of recent investigations support the predictions made by the correlations. Roberts et al. (1982b) and Cummins and Westrick (1983) reported $K_\ell a$ to increase with increasing liquid loading, with the effect less for compounds of lower volatility. Riojas et al. (1983) found $K_\ell a$ to decrease with decreasing gas loading; as volatility decreased, the solute's dependence on gas loading became more pronounced. Sensitivity of the mass transfer rate to gas flow is evidence of the importance of k_g.

This observed dependence of $K_\ell a$ on fluid loadings may be explained by looking at two aspects of packed towers: the effects of fluid loadings on interfacial area; and the hydrodynamic effects upon the mechanisms of mass transfer affecting k_ℓ and k_g.

1. Hydrodynamic Effects on Interfacial Area

The actual interfacial area is a function of the flow rates, fluid properties, and geometry and wetting characteristics of the packing. These factors interact to determine the area available for transfer and thus the efficiency of tower performance.

Ideally, the liquid distributed over the top of the packing flows in thin films over the entire packing surface all the way down

the tower. Actually the films tend to grow thicker in some places and thinner in others, sometimes forming small streams which flow in channels through the packing. The tendency towards channeling is greatest at low liquid flow rates, and much of the packing surface may not be wetted at all, effectively decreasing the area of transfer and thus the mass transfer coefficient. As the liquid flow increases, more of the packing surface is wetted. At sufficiently high liquid rates, all of the surface is wet and effective for transfer. Thus, interfacial area increases as more of the packing is wetted by increased liquid flow. At still higher liquid flows, a point is reached where an increase in liquid loading actually decreases effective area for transfer. Essentially, the average thickness of the cascading films increases and the system eventually approaches a flooded condition.

All of the correlations for interfacial area [Equations (47), (48), and (49)], including Onda's [Equation (46)], predict that the interfacial area, wetted or effective, increases with increasing liquid loading but is unaffected by gas loading. Experimentally determined values of effective area, a_e, and wetted area, a_w agree with the predicted dependence on liquid velocity; however, there is evidence that the assumption of independence of area on gas velocity might not be correct at low gas to liquid ratios or for small packings (Yoshida and Koyanagi, 1962).

Graphs of effective area presented by Shulman et al. (1955a) show a_e to be fairly independent of gas mass loading, G_m, in the low range; but as G_m increases, interfacial area begins to increase. This increase is most apparent for small packings, d_p less than 2.54 cm (1 inch).

Gas loading affects the flow of the liquid through the column and the area of contact between the two phases. At low gas flows the liquid moves downward through the packing uninfluenced by the gas. As gas flow increases, a point is reached where the gas flow impedes the flow of the liquid. Liquid begins to accumulate in the packing. Some accumulation is desirable at relatively low liquid loadings, as long

as the liquid continues to move through the packing being replaced by fresh liquid from above. This "moving hold-up," as it is often called, tends to increase the wetted area available for transport at low liquid loadings. If gas flow continues to increase, however, the liquid can no longer flow down the column, the column becomes flooded and transport stops. Interfacial area -- an important component of $K_\ell a$ -- increases as gas flow increases, until flooding occurs.

2. Hydrodynamic Effects on k_ℓ and k_g

According to the theoretical models of mass transfer, the rate of transfer of a compound through a fluid will depend upon the nature of the fluid motion. As the bulk fluid flow changes, the rate of transport from the bulk fluid to the interface changes. This may be due to a change in the thickness of the film layer, as pictured in the film model, or to a change in the rate of surface renewal, as presented in the penetration and renewal models. In either case, a change in the liquid or gas flow rate should change the respective transfer coefficient, k_ℓ or k_g.

The relative importance of changes in gas or liquid flows will depend upon the relative size of the gas- and liquid-phase resistances. For the most volatile compounds, gas resistance should be small, and thus $K_\ell a$ should be fairly independent of gas flow, with dependence on gas flow increasing as volatility decreases.

I. THE EFFECT OF PACKING SIZE AND SHAPE ON $K_\ell a$

The significance of packing size on effective area is not straightforward. Shulman's work indicates that a_e is dependent on the amount of liquid caught in stagnant areas of the packing, which may become ineffective for transfer. This hold-up is greatest for small packings. The increased hold-up tends to offset the advantage of greater surface area per volume gained by decreasing packing size. According to Shulman, effective area is greatest for intermediate packings, ~ 2.54 cm, but decreases for small packings, ~ 1.27 cm, due to liquid hold-up, and for larger packings, ~ 5.08 cm, due to less total area per volume (Yoshida and Koyanagi, 1962; Shulman et al.,

1955a). Onda et al. (1968) report that measured $k_g a$ values decrease for smaller packings. No explanation is given for this observation, but it could be due to a decrease in effective area.

Evaluation of liquid hold-up and its influence on effective interfacial area is quite complex. A certain degree of hold-up can actually increase the effective area due to an increase in the amount of packing that is wetted. As hold-up continues to increase, the thickness of the film on the packing increases and stagnant pools develop, thus, the amount of effective surface area per volume decreases. In effect, one would expect a_e to increase as liquid loading increases up to a maximum and then begin to drop off. In principle, either an extremely high liquid loading or gas loading could cause this drop-off.

The packing shape will affect the hydrodynamics in the column and thus the area of contact between the liquid and the gas. The existing correlations account for packing shapes in different ways: Onda uses the total surface area and the nominal packing size; Shulman uses total area and the diameter of an equivalent sphere; Sherwood and Holloway use the empirical packing factors α and n. The exact effects of packing size and shape have not been quantified.

J. STRIPPING FACTOR

The stripping factor, F_s, is commonly used in design of packed-tower stripping units and is defined as:

$$F_s = \frac{GH}{LRT_g} \text{ or } \frac{GH_c}{L} \tag{57}$$

The inverse of the stripping factor is found in the performance equation, Equation (8). The stripping factor characterizes the capacity for interphase transfer relative to equilibrium conditions. When values of F_s are less than one, there is a limited extent of stripping which cannot be surpassed even with an infinitely tall column (Roberts et al., 1982b).

K. PRESSURE DROP

Although pressure drop does not directly influence the mass transfer rate, it is an important consideration in design of packed towers. Pressure drop is an indication of the hydrodynamic conditions existing in the column and is an important factor in the economics of tower operation.

Generalized pressure drop correlations (e.g., Eckert's, given in Figure 18-39 of Perry and Chilton, 1973) allow estimation of the pressure drop across a tower for various flow rates, physical properties of the fluids, and packing types. The generalized plots have been developed as a practical aid to design, but due to differences in packing manufacture, the estimates are not exceptionally accurate (Treybal, 1980). Most packing manufacturers supply pressure-drop plots for their particular packings.

L. GENERAL PRINCIPLES OF DIFFUSION

The results of Gossett (1983), Sherwood and Holloway (1940), and Vivian and King (1964) reveal the strong effect of temperature on mass transfer in packed towers. As discussed previously and indicated in Table 1, this dependency stems in large part from the interactions of and temperature's effect on liquid viscosity, liquid-phase diffusivity, and Henry's constant. In the dilute solutions commonly encountered in air stripping of volatile organics, liquid viscosity is essentially the viscosity of water. While the theory of liquid viscosity is not well developed, reliable values for the viscosity of water are available. Despite its potentially significant role in determining mass transfer rates, viscosity cannot account for the differences in mass transfer coefficients between compounds at one temperature nor for the difference, if any, in the magnitude of the temperature effect on different compounds. Henry's constant and liquid-phase diffusivity are the parameters that must be examined for further insight into both the temperature sensitivity and the compound-dependent nature of mass transfer.

Accurate determination of Henry's constants as a function of temperature is one of the primary goals of this research study. A discussion of Henry's law and the effect of temperature on

gas/solution equilibria was presented previously in this report. This section examines what is known about diffusion in liquids to provide further insight into how temperature affects mass transfer.

Molecular diffusion, a consequence of the thermal agitation of individual molecules, results in a net transfer of mass within a single phase in an inhomogeneous fluid. Moleular diffusion is one of the controlling factors in interfacial mass transfer, although its importance is qualified in the presence of mixing by mechanical means or by convection. Under quiescent conditions, molecular diffusion is the sole means of mass transfer. Since it is caused by the movement of individual molecules, molecular diffusion is a dynamic, sporadic process that can only be measured quantitatively as a time and space average.

In dilute gases, each molecule's initial translation is independent of other molecules. Diffusion depends on velocities developed between moleular collisons and the subsequent transfer of momentum between randomly moving molecules (Reid and Sherwood, 1977), a process that has been accurately described through an advanced kinetic theory. (For more discussion, see Reid and Sherwood, 1977; Treybal, 1980; or Welty et al., 1976). In contrast, the dense, unstructured composition of liquids produces "soft, slow collisions, with constant exchange between translational and internal energy" (Hildebrand, 1971). Liquid diffusivities are orders of magnitude less than gas diffusivities. The former normally equal 0.5 to 2.[illegible] x 10^{-5} $cm^2 \cdot s^{-1}$ at 25°C; gas diffusivities range from 0.1 to 1.0 $cm^2 \cdot s^{-1}$ at atmospheric pressure (Sherwood et al., 1975). Liquid diffusion depends on the magnitude of attraction between molecules and on the energy required to move the molecules through the liquid (McCabe and Smith, 1976). The complex, chaotic nature of such molecular interactions has severely restricted the current understanding of the liquid state. Several theoreticians have attempted to describe liquid diffusion, using various idealized models, from Einstein's simplified approach that views molecules as hard spheres and emphasizes solute characteristics (Einstein, 1905), to Eyring's view that models diffusion as an activated process in which holes or moleular vacancies formed in the solvent govern the movement of solute molecules

(Glasstone et al., 1941). But even such theories, generally restricted to binary molecular diffusion, remain in a preliminary stage of development.

From a phenomenological perspective, the mass flux in one dimension is described by Fick's first law. Fick's law applies to dilute, binary systems under isothermal, isobaric conditions. Concentration differences must be small enough that the total density of the mixture is nearly constant. It is also implicity assumed that diffusion is not direction-dependent, a condition which holds for true solutions.

Since the mid-1940s, experimental measurement of diffusivities has been attempted with mixed success (Tuwiner, 1962). The experimental difficulties inherent in measuring diffusivities and the complexity of this molecular process have limited the development of generally applicable, accurate empirical expressions for diffusivities over a range of solute concentrations and solvents. However, moderately successful relationships have been developed that apply to binary diffusion in dilute, aqueous solutions. Diffusion, as discussed in the remainder of this study, refers to molecular diffusion in dilute, binary aqueous systems unless otherwise noted. "Diffusivity" or "diffusion coefficient" also is restricted to diffusivities under these conditions.

1. Temperature Dependence of Diffusivity

The effect of temperature is one of the factors explored in diffusion investigations; however, most studies have been restricted to the rather narrow range of from 10 to 40°C or less (Byers and King, 1966), with little data available above 30°C (Sherwood et al., 1975). The narrow range examined has thwarted attempts to establish a clearly defined temperature relationship, although these limited investigations have firmly established that increasing temperature significantly accelerates the rate of diffusion. The effect of temperature on diffusivity increases with the size of the diffusing particle, as established by Longsworth (1954) in his investigation involving compounds with molecular weights from 19 to 68,000. The work of

Hildebrand and Lamoreaux (1974) involving the diffusion of gases in carbon tetrachloride (CCl_4) supports this conclusion, as does Hayduk and Cheng's (1971) observation of increasing temperature dependence at low diffusivities.

Some investigators have presented their findings, using a linear relationship between temperature and diffusivity. Although this simple relationship appears to work for some compounds (for examples, see Houghton et al., 1962), it is clear that even over the short range of 15 to 25°C, a linear relationship does not precisely model the diffusion of argon or nitrous oxide in water (Duda and Vrentas, 1968). After analyzing much of the published data, Lusis (1971) concluded that, within the limits of experimental accuracy, a linear relationship is generally accurate over short temperature ranges.

A more commonly used temperature-diffusion relationship is an Arrhenius-type dependence first proposed by Eyring (Glasstone et al., 1941):

$$\ln D_{AB} = B_e \left(\frac{-\Delta E}{RT}\right) \tag{58}$$

where:

B_e = constant [= f(solute)];
R = universal gas constant;
ΔE = activation energy.

This is the same model most widely used to describe the temperature dependence of viscosity, discussed previously.

An Arrhenius-type dependence successfully modelled data for various gases in binary aqueous solutions from 10 to 60°C (Wise and Houghton, 1966) and for various hydrocarbons from 2 to 60°C (Bonoli and Witherspoon, 1968) and chlorinated hydrocarbons from 15 to 40°C in water (Caldwell and Babb, 1956). Witherspoon and Saraf (1965) noted some indication of changes in activation energy with temperature but could draw no definite conclusions due to the limits of experimental precision. An Arrhenius-type relationship was found to be insufficient for amides and some alcohols, although the relationship correlated data for ethanol and propanol (Gary-Bobo and Weber, 1969).

Using a nonexperimental approach, Ferrell and Himmelblau (1967) noted another restriction in the use of this type of relationship. The diffusivity calculated is very sensitive to the value of the activation energy. For nitrogen in water at 25°C, a 5 percent error in activation energy causes a 45 percent error in diffusivity. They concluded that this model should not be relied on for empirical use. Nevertheless, this is the temperature relationship recommended and used by many authors. In a thorough review of diffusion data Reid and Sherwood (1977) concluded this model can be effective over moderate temperature ranges, although it was suggested that a curve may more precisely model the relationship than a linear $\ell n\ D_\ell$ vs $1/T$ expression. Lusis (1971) recommended this form for conversions over moderate temperature ranges when two data points are known.

Hildebrand (1971, 1973), who has been credited with significantly adding to the understanding of the liquid state (Sherwood et al., 1975), strongly objects to the use of an Arrhenius-type dependence on theoretical grounds. The use of an activation energy term "implies the presence of barriers against freedom of flow, imagined as consisting of some sort of quasi-lattice structure, a notion that disregards the basic distinction between liquid and plastic flow..... All characteristics that distinguish crystals from liquids disappear upon melting..... Diffusion occurs by a succession of small displacements, not by leaps through barriers requiring energy of activation." He concluded that no "activation" is involved in diffusion, and temperature variations can be accurately and more simply represented by nonexponential functions.

Another approach employed in analyzing the temperature dependence of diffusion is to include the simultaneous changes in solvent viscosity. Many investigators have found that changes in viscosity and diffusivity cancel changes in temperature, resulting in a product, $D_\ell \mu_\ell / T$, which is constant for any solute. The Stokes-Einstein equation, based on hydrodynamic theory, states this relationship:

$$D_{AB} = \frac{RT}{6\pi \mu_\ell r_A} \tag{59}$$

where:

r_A = the radius of the spherical solute.

Originally derived to represent Brownian diffusion of colloids but widely applied to macromolecules in low-molecular-weight solvents, this equation uses a hard-sphere molecular model and neglects intermolecular forces. Although the Stokes-Einstein equation reportedly underestimates diffusivities by 40 to 50 percent and has practical limitations imposed on its use by the need to know molecular radii, $D_\ell \mu_\ell / T$ has been found to be relatively constant for any given solute and an accurate method for making temperature corrections to diffusivities in nonviscous systems when the solute and solvent are not of comparable size. Even in systems where $D_\ell \mu_\ell / T$ is not constant, assuming it is constant produces errors of less than 20 percent when extrapolating over 40°C (Lusis, 1971).

Some experts claim the temperature dependence of diffusivity can be explained entirely in terms of viscosity. As early as 1954, Longsworth reported, "Most of the twofold increase in diffusivity on raising the temperature from 1 to 25°C is due to a decrease in the viscosity of the solvent, less than 10 percent being due to the increase in the kinetic energy, kT, of the diffusing particle." More recently, Hayduk and Cheng (1971) tested the hypothesis that the diffusivity of a specific compound in any solvent would depend only on the solvent viscosity. Examining a range of solvents, temperatures, and solvent compositions, they found viscosity to be the only solvent parameter of concern and suggested that temperature, molar volume, collision diameter, etc., bear no strong relation to diffusivities or produce only second-order effects. Hayduk and Cheng found

$$D_{AB} = A^* \mu_\ell^{n^*} \tag{60}$$

where A* and n* are solute- and solvent-dependent constants, respectively, n* varying from -0.44 to -1.15 (n* = -1 for water). Some deviations from a single viscosity-diffusivity relationship exceeded their estimated experimental errors, but an equation of the form above correlated almost all data within approximately 20 percent. Other studies done at constant temperature and low viscosity reported a directly inverse proportionality between viscosity and diffusivity ($D_{AB} \propto \mu_\ell^{-1}$). This relationship fails in highly viscous

systems, where an approximate inverse relationship exists between diffusivity and viscosity to the 2/3 power (Cussler, 1976). A diffusivity-viscosity relationship with no other temperature correction factor has been used in some correlations, as will be discussed in a subsequent section.

No matter what relationship is used to determine changes in diffusivity over a range of temperatures, available data are too limited and inconsistent to allow formulation of a true diffusivity-temperature relationship. Over small temperature ranges, any of the foregoing temperature groups is nearly invariant. More data over wider ranges of temperature and viscosity are required to determine the validity and applicability of any relationship.

2. Solute Characteristics and Diffusion

In addition to the changes invoked on the diffusive process by temperature variation, diffusivity also depends strongly on the chemical characteristics of the solution. Generally, diffusivity changes with the size of the solute; a large molecule moves more slowly through the solution than a small one. The Stokes-Einstein equation expresses this relationship more precisely. With all other factors held constant, a modified version of this equation is:

$$D_{AB} \propto \frac{1}{\text{molecular diameter}} \tag{61}$$

With respect to its treatment of the solute, this equation has been found limited to large spherical molecules. According to Smith et al. (1980), gas molecules and most lower-molecular-weight organics fail to subscribe to this approximation; however, Wise and Houghton (1966) found diffusivities in the hydrocarbon series CH_4, C_2H_6, C_3H_8, and n-C_4H_{10} decrease linearly with increasing chain length.

The Stokes-Einstein equation fails in some situations because diffusion depends on changes in and factors other than solute size. The size of an isolated solute molecule will differ from its effective size in solution if it occurs in an "aggregated" form or as a solute-solvent association. The degree, magnitude, and effect of intermolecular forces are not well understood. The extent of solute-solvent association, in particular, remains an area of uncertainty and debate,

except for the general consensus that association tends to increase the effective molar volume and is likely to reduce the rate of diffusion. Evidence suggests that "a considerable degree of complexing occurs with most solutes in water" (Hayduk and Cheng, 1971). Additional insight into solute-solvent association is imperative, given the importance of diffusion in aqueous solutions both in water and wastewater treatment and in many chemical engineering processes.

Diffusion also varies with solute shape and concentration. The influence of molecular shape has rarely been addressed in the literature because of the difficulties isolating and studying this parameter. In one of the few investigations, Hayduk and Buckley (1972) obtained diffusivities for linear molecules approximately 30 percent greater than diffusivities for spherical molecules with the same molal volume at the normal boiling point. Many concentration studies have been performed; however, diffusivities investigated in this present study are limited to those at infinite dilution. Lusis (1971) reports this is a valid assumption for solute concentrations up to approximately 10 mole percent.

M. ESTIMATING LIQUID DIFFUSIVITIES

Despite the difficulties of experimental measurements and the somewhat contradictory and confusing experimental results, empirical correlations have been developed for predicting liquid-phase diffusivities. Limited essentially to diffusion in infinitely dilute, binary solutions with no solute-solvent interaction, all correlations relate diffusivity to temperature, viscosity, and molecular size. The relationships established in the Stokes-Einstein equation are basic to the development of many correlations.

1. The Wilke-Chang Correlation

The most widely used correlation is essentially an empirical modification of the Stokes-Einstein equation developed by Wilke and Chang in 1955. Their analysis of available data generally supported the Stokes-Einstein relationship, which they simplified to:

$$F = T/(D_{\ell}\mu_{\ell}) \qquad (62)$$

where:

F = diffusing factor.

They determined that, for a given solvent, F was a smooth function of the solute's molar volume. In attempts to determine the effect of the solvent molecular weight, the problem of considerable scatter in the data was effectively alleviated by introducing an "association parameter" to define the effective molecular weight of the solvent for associating liquids such as water. The resulting correlation is:

$$D_\ell = \frac{7.48 \times 10^{-8} (XM_w)^{0.5} T}{\mu_\ell V_b^{0.6}} \qquad (63)$$

where:

D_ℓ = diffusivity ($cm^2 \cdot s^{-1}$);
μ_ℓ = solvent viscosity (cP);
V_b = molar volume of the solute at its normal boiling point (cm^3/mol);
M_w = solvent molecular weight;
X = association factor for the solvent
= 2.6 for water.

Wilke and Chang reported an average error of approximately 10 percent for their correlation with water as the solvent. The Wilke-Chang correlation with X = 2.6 is used in this report to estimate liquid-phase diffusivities in the Onda correlation for mass transfer coefficients.

2. The Scheibel Correlation

Scheibel (1954) developed an equation that was essentially a modification of an earlier, but similar, Wilke-Chang correlation. In an attempt to increase reliability as the solute-to-solvent size ratio decreased (an area where the first Wilke-Chang correlation failed) and to eliminate the need for an association parameter, Scheibel developed the following relationship, valid down to a solute molar volume equal to or greater than the solvent's if the solvent is water:

$$D_\ell = \frac{K T}{\mu_\ell V_b^{1/3}} \qquad (64)$$

where:

$$K = (8.2 \times 10^{-8}) \left[1 + \left(\frac{3V_a}{V_b}\right)^{2/3}\right];$$

V_a = solvent molar volume at its normal boiling point.

This expression is said to be reliable for $V_b \geq 2\ V_a$ (or $V_b \geq V_a$ if water is the solvent). When water is the solvent and $V_b < V_a$, $K = 25.2 \times 10^{-8}$. Scheibel retained $V_b^{1/3}$ as in the original Wilke-Chang correlation.

3. The Othmer-Thakar Correlation

Othmer and Thakar also published a correlation around the same time as Wilke/Chang and Scheibel (Othmer and Thakar, 1953). In their independent analysis, they discovered that diffusion in dilute aqueous solutions could be correlated, using only the solvent viscosity for temperature corrections. They found the slope of log D_ℓ versus viscosity varied from -1.07 to -1.15, with a fair average equal to -1.1. In their correlation, published prior to the Wilke-Chang correlation [Equation (63)], they related the rate of diffusion to the solute's molar volume to the 0.6 power, resulting in the following equation:

$$D_w = \frac{14.0 \times 10^{-5}}{\mu_w^{1.1}\ V_b^{0.6}} \tag{65}$$

where:

D_w = diffusivity in an aqueous solution ($cm^2 \cdot s^{-1}$);

μ_w = viscosity of water (cP).

This equation was developed primarily for estimating diffusivities in water. Unlike the previous correlations, its use with other solvents is limited.

4. Hayduk and Laudie Revisions

The three correlations presented above were developed from data obtained primarily prior to 1950. In 1974, Hayduk and Laudie reevaluted all three correlations using only post-1950 aqueous diffusivity data. Making no changes in Scheibel's correlation, Hayduk and Laudie found the average error of the Wilke-Chang correlation

could be reduced by decreasing the association parameter for water from 2.6 to 2.26. They also modified* the Othmer-Thakar correlation to:

$$D_w = \frac{13.26 \times 10^{-5}}{\mu_w^{1.4} \, V_b^{0.586}} \qquad (66)$$

5. Summary of Diffusivity Correlations

Other correlations have been developed, often in an attempt to broaden the range of applicability to include conditions such as diffusion in viscous liquids, in organic solvents, or when water is the solute, where the correlations presented here tend to fail. These correlations, including those developed specifically in an attempt to improve diffusivity estimates in dilute aqueous solutions, tend to be less accurate or less convenient than the correlations presented above. The Wilke-Chang, Othmer-Thakar, and Scheibel correlations and the Hayduk-Laudie revisions are generally acknowledged to be the most reliable and easiest to use in dilute aqueous solutions. All of these correlations predict virtually identical diffusivities; the Scheibel correlation, which predicts the most extreme values, tends to be only 2 to 2-1/2 percent higher than the other expressions (Hayduk and Laudie, 1974).

Various reviewers and investigators report average errors of between 10 and 20 percent for each correlation reviewed. In isolated instances, however, each correlation has differed from experimental data by as much as $\pm$ 30 percent (Reid and Sherwood, 1977). Different reviewers prefer different correlations. The Wilke-Chang correlation appears to be the most widely used, but many recommend Othmer and Thakar's or Hayduk and Laudie's more convenient correlations for diffusion in dilute aqueous solutions. According to a review by Lusis

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* In their published equation, they report $\mu_w^{-1.4}$; however, in the discussion of their analysis they report, ".... log D was found to vary linearly with log μ with lines having an average slope determined as -1.14" (our emphasis). In future evaluations of this Hayduk-Laudie correlation (e.g., Reid and Sherwood, 1977), 1.4 and not 1.14 has been used as the exponent.

(1971), the Wilke-Chang correlation has been a poor choice for unsaturated hydrocarbon solutes; however, Witherspoon and Bonoli (1969) support its use for aromatic and cycloparaffin hydrocarbons in water, and Huq and Wood (1968) report that the Wilke-Chang correlation best represents experimental results for the diffusion of ethylene in water.

Some of the discrepancies encountered in diffusivity data could result from estimations of the solute's molar volume at its normal boiling point (V_b). Experimental measurements, while the most reliable, are not generally available. The most common of several methods developed for estimating molar volumes is the LeBas additive method (Perry and Chilton, 1973). With this method (used in this study), volume contributions for each element in a compound are added together. This method is a refinement of Schroeder's rule, an earlier additive method based on the number of carbon, hydrogen, oxygen, and nitrogen atoms, with adjustments for double bonds. Schroeder's method was later expanded to include halogens, sulfur, and triple bonds.

Reid and Sherwood (1977) compared the LeBas and Schroeder methods with experimental molar volumes. For the compounds examined, LeBas molar volume estimate deviations from experimental values ranged from -21.5 to 11 percent; Schroeder molar volume errors varied within $\pm$ 12 percent. Molar volumes for the compounds of interest in this study calculated using both methods are presented in Table 2. The order is the same for these compounds with either method, and differences between methods are not judged to be of practical significance. With the exception of tetrachloroethylene, Schroeder estimates are slightly higher than LeBas estimates. Hayduk and Laudie (1974) and Himmelblau (1964) cite the use of estimated molar volumes as one reason for the deviation between experimental and calculated diffusivities. Both report lower average errors in diffusivity correlations if true molar volumes are used. The use of estimates should yield only slightly less accurate results (Hayduk and Laudie, 1974).

The use of different diffusivity correlations yields a range of diffusivity values for the organics specific to this study. Table 3 shows diffusivity values calculated using the various correlations

TABLE 2. LIQUID MOLAR VOLUMES AT THEIR NORMAL BOILING POINTS

Compound	Le Bas Method ($cm^3 \cdot mol^{-1}$)	Schroeder Method ($cm^3 \cdot mol^{-1}$)
Methylene chloride	65.4	70.0
Chloroform	83.3	87.5
Trichloroethylene	98.1	101.5
1,1,1-Trichloroethane	105.5	108.5
Tetrachloroethylene	116.0	115.5

TABLE 3. AQUEOUS-PHASE DIFFUSIVITIES CALCULATED USING VARIOUS CORRELATIONS[a]

Compound	Temperature °C	Hayduk & Laudie	Othmer & Thakar	Wilke-Chang (X = 2.26)	Wilke-Chang (X = 2.6)	Scheibel
Methylene Chloride	10	0.777	0.849	0.832	0.893	0.841
	20	1.13	1.12	1.12	1.21	1.14
	30	1.55	1.46	1.46	1.57	1.48
Chloroform	10	0.674	0.734	0.720	0.772	0.721
	20	0.977	0.984	0.972	1.04	0.974
	30	1.35	1.26	1.26	1.35	1.27
Trichloro-ethylene	10	0.612	0.666	0.653	0.700	0.652
	20	0.888	0.892	0.881	0.945	0.881
	30	1.22	1.15	1.15	1.23	1.14
1,1,1-Trichloro-ethane	10	0.586	0.637	0.614	0.670	0.624
	20	0.850	0.854	0.830	0.905	0.843
	30	1.171	1.10	1.18	1.18	1.10
Tetra-chloro-ethylene	10	0.554	0.602	0.590	0.633	0.590
	20	0.804	0.806	0.797	0.855	0.797
	30	1.11	1.04	1.04	1.11	1.04

[a] Le Bas method used in all cases for molar volume estimations.

and LeBas molar volumes. All correlations predict methylene chloride to have the highest diffusivity, followed in descending order by chloroform, trichloroethylene, 1,1,1-trichloroethane, and tetrachloroethylene. It is apparent that, as previously mentioned, only small variations exist among predictions made using the various correlations for any given compound and temperature.

In conclusion, established correlations are useful for obtaining rough estimates of diffusivities; however, their reported accuracy ($\pm$ 10-30 percent) is insufficient to make meaningful any small, predicted differences in diffusivities for compounds as similar as these organics of concern in groundwater contamination or to determine absolute changes in diffusion rates over the temperature range of interest. As pointed out by Lusis (1971), the approximately 15 percent change in diffusivity from 0 to 10°C is often less than the error involved in the estimate. Additional problems in comparing diffusion rates arise since none of the correlations account for observed differences in the temperature dependence of diffusivities for different solutes in the same solvent (Shrier, 1967). While for many binary systems prediction methods are surprisingly accurate, "it is disconcerting to find that for some other data, for unexplained reasons, large deviations are observed" (Hayduk and Cheng, 1971). These abnormalities preclude the use of such correlations in situations requiring accurate and precise diffusivities. Experimentally determined values are considered the most reliable.

N. METHODS FOR MEASURING LIQUID-PHASE DIFFUSIVITIES

The slowness of the diffusion process and its dependency on concentration render experimental measurement of diffusivities mathematically and/or mechanically complex. Additional complications arise due to the ease with which thermal or mechanical convection currents, vibrations, and density differences can mask molecular diffusion. Limitations in determining concentrations or concentration differences also restrict the reliabilty and ease of diffusivity measurements.

Steady-state diffuson methods tend to have simpler mathematical analysis and less complex equipment. Two steady-state methods,

diaphragm cells and liquid jets, have been recommended for low-solubility compounds (Ferrell and Himmelblau, 1967). The diaphragm cell method employs a porous glass diaphragm with solution chambers on each side. Diffusion proceeds through the pores of the diaphragm, resulting in a net transfer of mass from the high concentration side of the disk to the low concentration side. When the volume on each side of the diaphragm is large and the solutions are stirred to ensure uniform concentrations, then transfer across the diaphragm is essentially steady-state. One drawback to this method is the need to calibrate the cell with a solute of known diffusivity, since the effective area and length of the diffusion path are not known. In general, however, accurate results can be achieved using this relatively simple method.

Liquid jet systems have been used for low-solubility compounds and gas-liquid systems. The solute gas is absorbed in a laminar-flowing solvent liquid stream of known geometry. The solute's diffusivity is calculated from the observed absorption rate. Solvents flowing over spheres or rotating drums have been used; however, the most successful technique uses a laminar-falling jet. Although more elaborate equipment is required than with the diaphragm cell, the mathematical analysis involved is the simplest of any method. The primary limitation of this method is its dependence on accurately known solubilities. A 1 percent error in solubility data produces approximately a 2 percent error in the diffusivity (Unver and Himmelblau, 1964). Since solubility data generally exhibit considerable scatter, the accuracy of this method is unknown, although apparently reliable results have been obtained for various gas-liquid systems.

The capillary tube method, an unsteady-state method developed by Wang (1951), determines diffusivities using a 2- to 6-cm capillary tube of uniform interior diameter. The tube is sealed on one end and lowered, sealed-end first, into a constant-temperature, agitated bath until the open end is covered. After 4 or 5 days the tube is withdrawn, and the diffusivity is determined by measuring the concentration gradient in the tube or, as is more common, by measuring the total amount passing into or out of the tube. As with the diaphragm cell method, proper stirring is essential. Stirring that is too rapid

causes convection within the tube and at the open end; if stirring is too slow, the stagnant layer of bath solution at the tube's end increases the effective length of the tube. Experimental errors are caused by volume changes from solvent diffusion into the tube and errors in immersing and withdrawing the tube. Reliable results have been obtained with this method; however, this method is generally not competitive with the diaphragm cell or the optical method discussed below.

Optical methods, especially the Gouy interferometer, are the most accurate means of measuring diffusivities. Two beams projected from a single source of light pierce the diffusion cell at two levels and are brought to a common focus as they emerge from the cell. The progress of diffusion is recorded by the change of refractive index of the liquid as a function of time and distance. This technique is especially good with concentrated solutions, as small concentration differences can be determined. The main limitation is establishing reproducible initial conditions. This delicate technique requires expensive equipment and complex mathematical analysis; however, it produces the most reliable results and is an absolute method (no calibration is required).

The combination of availability or ease of obtaining equipment, simplicity of experimental construction and operation, accuracy, and cost make the diaphragm cell method of measuring diffusivities the best method for this research.

1. The Diaphragm Cell Method

First developed by Northrup and Anson (1928) and brought to the stage where it was recognized as an exact method by Stokes (1950a), the diaphragm cell has become a common and accepted method for measuring diffusivities. This method relies on confining diffusion to the pores of a fritted glass diaphragm and measuring changes in concentrations on each side of the diaphragm with time. Since diffusion in liquids is a slow process, and changes in concentrations must be determined accurately, diaphragm cell experiments generally last several days. As with all diffusion

experiments, the elimination of thermal and mechanical convection is essential in determining molecular diffusivities.

Diaphragm cells have been used successfully with solution chambers on either side of the fritted disk of from 10 ml to 200 ml and with pore diameters ranging from 1 to 20 micrometers (μm). Pores must be small enough to avoid gross streaming of fluid, but large in comparison with molecular dimensions so that conditions are comparable to free diffusion (i.e., molecules collide with each other more than with the walls of the pores). Pore diameters of 2-5 μm or 15-20 μm are the most common and have been shown to eliminate bulk flow -- except with the coarser diaphragm when appreciable differences in density exist between the two chambers (Gordon, 1945). Emanuel and Olander's (1963) research using saturated $CuSO_4$ in water and 5 μm diaphragm pores revealed that mass flux due to density differences was 100 times greater than that caused by molecular diffusion. Finer diaphragms eliminate bulk flow but are more susceptible to contamination, clogging, and surface transport along the walls of the pores.

Vertical diffusion cells (with the diaphragm-oriented horizontally) minimize transfer due to density currents and have been used traditionally in diaphragm cell experiments. Since the 1960s, however, horizontal cells have been used successfully (Holmes, 1960; Byers and King, 1966; Chandrasekaran and King, 1972). Horizontal cells are more susceptible to bulk flow from density currents than vertical cells. Densities in the two cell chambers that are significantly different tend to yield apparent values for diffusivities which greatly exceed the molecular values. Very dilute aqueous systems were employed in this present research. Since densities of the two solutions were essentially equal in this investigation, horizontal cells were used to facilitate experimental construction and procedures.

To minimize errors caused by bulk flow, experimenters would be encouraged to minimize density differences between the two solution chambers; however, decreasing the concentration difference between the sides increases the potential error in the diffusivity calculated. Stokes' (1950b) mathematical analysis of the equations involved

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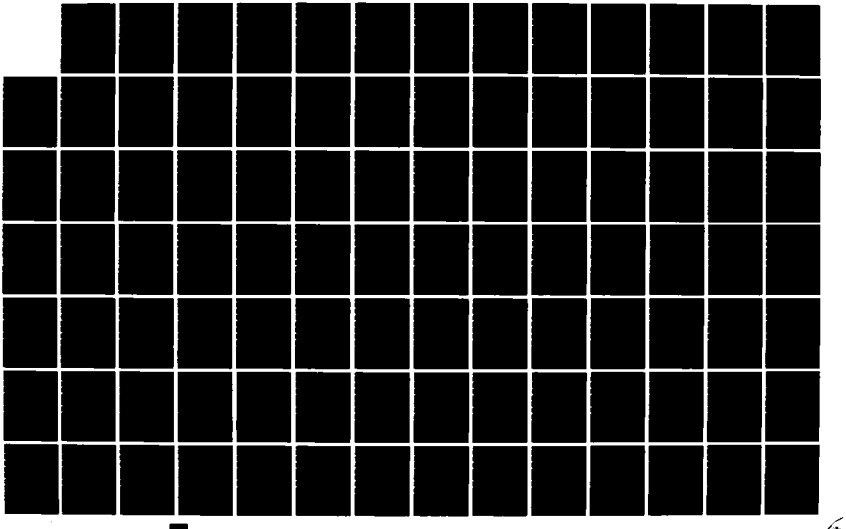

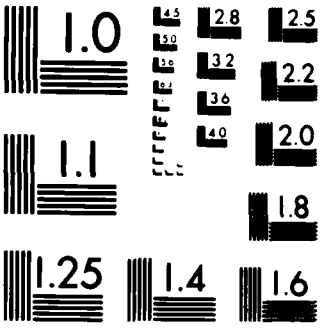

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revealed the multiplying effect of errors in measured concentrations. For example, if the initial concentration ratio between the two chambers equals two, the resultant error in the calculated diffusivity may be 10 times the error in measured concentrations. The potential error in diffusivity decreases as the initial concentration ratio increases. If one side of the diffusion cell contains no solute initially, the multiplying factor in the relative potential error caused by concentration measurements is scarcely greater than two. Errors induced by concentration measurements can also be minimized by allowing diffusion to proceed until the final concentration difference between the two chambers equals approximately half the initial difference.

A key element in diaphragm cell design is that the volume of the pores is much less than the volume of either solution chamber. Then the change in concentration with time is much less than the change with position in the diaphragm, and mass transfer across the diaphragm is, for all practical purposes, steady-state. When the solution in the diaphragm pores is less than 10 percent of the total cell volume, the maximum error due to the assumption of steady-state within the diaphragm is less than 3 percent (Cussler, 1976). Generally, the volume of the diaphragm is less than 1 percent of the total volume (Mills et al., 1968).

In the classic diaphragm cell equation for calculating diffusivities, the diaphragm is viewed as equivalent to a collection of parallel pores of average effective length, ℓ, and total effective cross-sectional area, A. The equation as presented by Gordon (1945) is:

$$\ell n \frac{\Delta C_o}{\Delta C_t} = B_G \, Dt \qquad (67)$$

where:

ΔC_o = concentration difference between the two solution chambers at time t = 0;

ΔC_t = concentration difference between the two solution chambers at time t;

B_G = diffusion cell constant = $\frac{A}{\ell}\left[\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right]$;

D = diffusivity measured using the diaphragm cell ($cm^2 \cdot s^{-1}$);

t = time (s);

V'_ℓ, V''_ℓ = liquid volume in each solution chamber (cm^3).

Derivation of this equation assumes:

- pseudo-steady-state conditions as described above;
- an initial, linear concentration gradient across the diaphragm;
- approximately equal chamber volumes to the extent that (C' + C") remains constant; and
- transfer across the diaphragm is limited to molecular diffusion.

The area (A) and length (ℓ) of the diffusion path across the diaphragm cannot be determined directly for each cell. Hence, the diaphragm cell method is not an absolute method but one requiring calibration with a solute of known diffusivity to determine the cell constant. The method is no more accurate than the standard used for calibration. Stokes (1951) determined precise diffusivities of KCl in water at concentrations up to 4M, expressly for use in the calibration of diaphragm cells. This data have been used extensively in diaphragm cell experiments. Stokes (1950b) also performed an extensive study to obtain accurate diffusivities of eight other electrolytes in aqueous solutions. Although used to a lesser extent than his data for KCl, Stokes' data for HCl has been used successfully in diaphragm cell calibration. Byers and King (1966) calibrated cells using 0.1N KCl and obtained cell constants virtually identical to those obtained years earlier by Holmes (1960) using 0.2N HCl.

Calibration can introduce errors if done improperly; however, the cell constant can also correct for consistent departures from underlying assumptions. This attribute is especially important with respect to cell volume. To a certain extent, all diaphragm cell experiments are based on equal chamber volumes, a condition not always

realized in the cells used in experiments. As pointed out by Gordon (1945), if the liquid in one chamber is 1 percent greater by volume than that in the other, and the calibration experiment is allowed to proceed until the final concentration difference between chambers is 40 percent of the initial concentration difference, this volume difference creates an error in the cell constant equal to 0.35 percent. However, if the volume difference is due to cell geometry and not to experimental error in filling the chamber, this error is accounted for in all experiments by the cell factor and the error is entirely negligible. A random error, which cannot be absorbed by the cell constant, is much more serious than a consistent error.

In calibrating cells, conditions must be similar to those of the actual experiments. Large temperature differences between the calibration run and the actual diffusivity experiments should be avoided, as the cell constant varies with temperature. Temperature differences of 5°C between calibration and actual experiments have been used with no ill effects. The viscosity of the calibration and experimental solutions should be similar. Errors are also minimized by running the calibration experiments for the same length of time as the actual runs (Ertl et al., 1974). With respect to concentrations, however, no calibration should be performed below 0.1N. At lower concentrations, anomalous surface effects across the face of the diaphragm become prominent when diffusion involves electrolytic solutes (Stokes, 1951).

Reliable and accurate results are more readily obtained when the solution in each chamber is mechanically mixed. Stirring insures uniform composition of the solutions on each side of the diaphragm. Equally important, stirring minimizes stagnant layers shown to exist adjacent to the diaphragm. In addition to other factors not well understood, the intensity of stirring and the viscosity of the solution govern these layers, which in turn affect the cell constant. The cell constant has been shown to vary with the stirring speed up to an empirically-determined critical speed where the cell constant becomes independent of stirring speed. Depending on cell geometry, this critical speed may be as low as 50 rpm (Stokes,

1950a) or much higher. With horizontal diaphragms, many investigators have used stirring rates greater than 120 rpm; rates of 300 rpm have been used with vertical diaphragms.

The external mass transfer resistance due to these stagnant layers can be accounted for in diaphragm cell equations by 2D/kA' as follows (Holmes, 1960; 1963):

$$\ell n \frac{\Delta C_o}{\Delta C_t} = B_H Dt; \qquad (68)$$

where:

$$B_H = \left[\frac{1}{V_{\ell}'} + \frac{1}{V_{\ell}''}\right] \left[\frac{1}{2D/kA' + \ell/A}\right];$$

k = average mass transfer coefficient through each stagnant layer ($cm \cdot s^{-1}$);

A' = effective stagnant area for transfer (cm^2).

Thus, in addition to stirring speed, these laminar layers will be infuenced by viscosity and diffusivity. This led Holmes (1963) to doubt the validity of the cell constant's independence of stirring above a critical speed. Using a specially designed cell, Holmes found that if 2D/kA' is large compared with ℓ/A, the mass transfer resistance term must be included in the cell constant. However, for many systems, operation above the critical stirring speed renders 2D/kA' negligible with respect to ℓ/A. Errors may result in systems of high viscosity and low diffusivity or with highly porous diaphragms, but generally (2D/kA' + ℓ/A) varied less than 0.2 percent with fluid properties. For most stirred, aqueous systems, no corrections to the cell constant determined by calibration using dilute HCl or KCl are necessary or warranted. If the cells are not stirred, the cell constant may vary with fluid properties.

The diffusivity measured by tne diaphragm cell is actually an integral diffusivity resulting from a range of concentrations and not the differential diffusivity valid for a specific concentration. No correction is necessary for small changes in concentration or with very dilute solutions; the diffusivity measured can be assumed equal to the differential value at the approximately-constant concentration in the first case, and equivalent to the diffusivity at infinite

dilution in the second. At mole fractions less than 0.002, the integral diffusivity determined is essentially equal to the diffusivity at infinite dilution (Hayduk and Laudie, 1974).

The diaphragm cell equations presented earlier are not entirely valid for this study because of cell modifications made for sampling purposes. As described later in more detail, headspace sampling ports sealed with silicone/Teflon® septa and plastic screw caps were added to each chamber to allow sampling and determination of solution concentrations via headspace gas chromatography. The addition of gas headspaces on both sides of the diaphragm necessitated modification of the equations developed by Gordon and Holmes. In deriving these equations, the following conditions were assumed:

- Transport through the diaphragm is assumed to occur by molecular diffusion with additional resistance to transfer due to stagnant layers along each face of the diaphragm.
- Bulk flow or surface transport along the walls of the pores is neglected.
- Volume changes during the experiment are neglected.
- The solutions are assumed uniform in composition up to the entrance to the pores.
- The volume of the pores is neglected.
- Psuedo-steady-state conditions exist across the diaphragm.
- Instantaneous equilibrium exists between the liquid and the gas phases.

The solute mass diffusing through the diaphragm during time dt is (Holmes, 1960):

$$\frac{dM}{dt} = \frac{C'_\ell - C''_\ell}{\frac{2}{kA'} + \ell/DA} \tag{69}$$

where C'_ℓ and C''_ℓ are the liquid-phase solute concentrations in the two chambers separated by the diaphragm ($mol \cdot cm^{-3}$). A mass balance on

each side of the diaphragm yields:

$$\text{Side 1:} \quad V'_\ell \, dC'_\ell + V'_g \, dC'_g + \frac{C'_\ell - C''_\ell}{\frac{2}{kA'} + \frac{\ell}{DA}} \, dt = 0 \tag{70}$$

$$\text{Side 2:} \quad V''_\ell \, dC''_\ell + V''_g \, dC''_g + \frac{C''_\ell - C'_\ell}{\frac{2}{kA'} + \frac{\ell}{DA}} \, dt = 0 \tag{71}$$

where:

V'_g, V''_g = headspace volumes in each chamber (cm^3);

C'_g, C''_g = headspace concentrations in each chamber ($mol \cdot cm^{-3}$).

Substituting $C_g = H_c C_\ell$ and $\theta = \frac{2}{kA'} + \frac{\ell}{DA}$ results in:

$$\text{Side 1:} \quad \left(\frac{V'_\ell}{H_c} + V'_g\right) dC'_g + \left(\frac{C'_g - C''_g}{H_c \theta}\right) dt = 0 \tag{72}$$

$$\text{Side 2:} \quad \left(\frac{V''_\ell}{H_c} + V''_g\right) dC''_g - \left(\frac{C'_g - C''_g}{H_c \theta}\right) dt = 0 \tag{73}$$

Letting

$$Q = \frac{V'_\ell}{H_c} + V'_g \; ; \qquad S = \frac{V''_\ell}{H_c} + V''_g$$

and adding Equation (72) to Equation (73) yields:

$$\int_{C'_{go}}^{C'_g} Q \, dC'_g + \int_{C''_{go}}^{C''_g} S \, dC''_g = 0 \tag{74}$$

or

$$Q[C'_g - C'_{go}] = -S[C''_g - C''_{go}]. \tag{75}$$

Rearranging produces

$$C''_g = -\frac{Q}{S}[C'_g - C'_{go}] + C''_{go} \tag{76}$$

which can be substituted into Equation (72) to yield

$$QH_c \theta dC'_g + [C'_g - C''_{go} + \frac{Q}{S}(C'_g - C'_{go})]dt = 0 \tag{77}$$

Rearranging produces

$$QSH_c \theta \int_{C'_{go}}^{C'_{gt}} \frac{dC'_g}{(QC'_{go} + S\,C''_{go}) - (Q + S)C'_g} = \int_{t_o}^{t} dt \tag{78}$$

which yields upon integration

$$-\frac{Q\,S\,H_c\,\Theta}{Q+S}\,\ell n\,\left[\frac{(Q\,C'_{go}+S\,C''_{go})-(Q+S)C'_{gt}}{(Q\,C'_{go}+S\,C''_{go})-(Q+S)C'_{go}}\right]$$

$$=t-t_o=\Delta t \qquad (79)$$

Substituting Equation (76) and rearranging results in

$$\ell n\,\left[\frac{C''_{gt}-C'_{gt}}{C''_{go}-C'_{go}}\right]=\ell n\,\left[\frac{\Delta C_t}{\Delta C_o}\right]=\frac{-(Q+S)}{QSH_c\Theta}\,\Delta t \qquad (80)$$

or

$$\ell n\,\left[\frac{\Delta C_t}{\Delta C_o}\right]=\frac{-\Delta t}{\theta}\,\left[\frac{1}{V'_\ell+H_c\,V'_g}+\frac{1}{V''_\ell+H_c\,V''_g}\right] \quad . \qquad (81)$$

Substituting for θ and rearranging yields the final form of the equation:

$$\ell n\,\frac{\Delta C_o}{\Delta C_t}=BDt\left[\frac{1}{V'_\ell+H_c\,V'_g}+\frac{1}{V''_\ell+H_c\,V''_g}\right] \qquad (82)$$

where:

$$B=\frac{1}{\frac{2D}{kA'}+\frac{\ell}{A}} \quad .$$

0. SUMMARY

Performance of packed towers depends upon tower design, operating conditions, and properties of the chemicals being removed, which include H and $K_\ell a$. Inadequate data -- and methodologies for obtaining reliable data -- exist with respect to Henry's constant. $K_\ell a$ is a complex quantity affected by design and operating factors, packing type and size, and properties of the fluids and the solutes to be removed. Factors which influence $K_\ell a$ (according to the Onda correlations) can be summarized as:

Factor	Affects $K_\ell a$ via:
Compound	D_ℓ, D_g, H
Temperature	D_ℓ, D_g, H, μ_ℓ, μ_g, ρ_ℓ, ρ_g, σ
Packing	a_t, d_p, σ_c
Fluid Mass Loadings	L_m, G_m

There is adequate basis in chemical engineering practice to design packed towers for stripping of volatile organics from contaminated water supplies. The design methodologies, however, require knowledge of Henry's constant and the mass transfer coefficient for the compound being stripped. Empirical correlations from the chemical engineering literature for estimating $K_\ell a$ have proven to be reliable in small-scale laboratory studies, but application to large-scale facilities is as yet very limited. Before effective designs can be accomplished it is necessary to demonstrate the methodology in larger units using a variety of packings and a wide range of liquid and gas flows. Additionally, use of the $K_\ell a$ correlations requires knowledge of liquid-phase diffusivities, data generally lacking for compounds of interest. Empirical D_ℓ correlations must be employed and -- as with $K_\ell a$ estimations -- the accuracy of these diffusivity estimates should be experimentally evaluated.

SECTION III

GENERAL PROCEDURES

A. PROGRAM OF STUDY

This research project was conducted in several separate phases which address the numerous objectives defined earlier. Compounds studied included: tetrachloroethylene; 1,1,1-trichloroethane; trichloroethylene; chloroform; and methylene chloride. Some equilibrium studies were also conducted,using o-dichlorobenzene.

Equilibrium studies were first performed to assess the effects of temperature, ionic strength, and organic mixtures on Henry's constant. Initially, the batch stripping column method of Mackay et al. (1979) was employed. When unexpected and peculiar results were obtained in some of the mixture studies, a novel technique -- termed "EPICS" -- was developed. Thus, an additional objective of this study phase was the evaluation of the EPICS technique and its comparison to other methods of Henry's constant determination.

In a second major phase of study, partially successful attempts were made to evaluate some of the existing correlations for liquid-phase diffusivity, an important input parameter to the various $K_\ell a$ correlations. A diaphragm-cell method was employed to measure D_ℓ values for the five primary study compounds.

In a third major phase of study, overall volumetric mass transfer coefficients ($K_\ell a$ values) were measured for the five primary volatiles listed above. A 3.05-meter (10-foot) x 44.5 cm ID (17.5-inch) packed tower was employed, with 2.44 meters (8 feet) of packing. To expedite experimentation, mixtures of the five volatile compounds were generally used -- often in the presence of methanol, used to dissolve the study compounds. In a preliminary study, it first had to be demonstrated that these mixtures do not affect the $K_\ell a$ values of the individual compounds. Subsequently, $K_\ell a$ values were determined for the five compounds using seven packings, varying temperatures from 10° to 30°C, and over wide ranges of gas and liquid loadings. These data were used to evaluate the accuracy of the Onda correlations for predicting $K_\ell a$ values.

B. SAMPLE ANALYSIS

Although directed toward the common objective of modelling air-stripping processes, the separate studies comprising this research project are somewhat diverse in nature. Therefore, experimental procedures specific to each study are detailed in a separate chapter devoted to procedures, results, and discussion of each. In this chapter, only procedures of sample analysis common to all phases of study are discussed.

1. Headspace Chromatography

The technique chosen in this study to analyze the concentrations of liquid samples is a variation of "headspace gas chromatography." This technique was proposed by Dietz and Singley (1979) as a simple method for determining the concentrations of volatile compounds in solution. It involves placing a known volume of solution in a closed serum bottle with a gaseous headspace, and allowing the system to reach equilibrium. Assuming that Henry's law holds, a simple mass-balance analysis shows that the resulting equilibrium gas-phase concentration is directly proportional to the initial liquid concentration.

The mass of volatile chemical contained by the serum bottle can be expressed as the product of the initial liquid concentration ($C_{\ell o}$) and the liquid volume (V_ℓ):

$$M = C_{\ell o} V_\ell \tag{83}$$

After equilibrium with a headspace, the total mass is partitioned between gas and liquid phases as:

$$M = C_\ell V_\ell + C_g V_g = C_g V_\ell / H_c + C_g V_g \tag{84}$$

Setting Equations (83) and (84) equal to each other and solving for the initial liquid concentration gives:

$$C_{\ell o} = (V_g/V_\ell + 1/H_c)C_g \tag{85}$$

Equation (85) shows that if V_ℓ, V_g, and H_c are constant for all systems, then there will be a uniform constant of proportionality

between equilibrium headspace gas concentration and initial, aqueous concentration.

None of the experimental methods employed in this research requires knowledge of the absolute aqueous concentration. Data analysis of batch air stripping for Henry's constant measurement [via Equation (16)], of the diaphragm method for measuring D_ℓ [via Equation (68)], and of packed-tower air stripping [via Equation (8)] all rely merely upon ratios of concentrations sampled over time or space. As long as there is a uniform constant of proportionality within a particular experimental run between actual, aqueous concentration and some raw measure of concentration (such as headspace chromatographic peak height) then data analysis can be performed, and the actual constant of proportionality need not be known.

The assumptions necessary to insure proper application of headspace chromatographic data in these present studies include: that V_ℓ and V_g are constant among sample bottles; and that the concentrations of all samples are within the range where Henry's law is valid so that Henry's constant is, in fact, constant. In addition, the peak height response of the gas chromatograph to headspace concentration should also be linear. These assumptions were checked through preparation of dilution curves for each compound, as described in Section III.D.

The headspace chromatographic analysis of aqueous samples was carried out as follows. Samples of 25 ml volume were poured into 120 ml serum bottles with a minimum of agitation, and immediately sealed with Teflon®-lined rubber septa and aluminum crimp caps. The serum bottles were allowed to reach ambient temperature and were shaken for 15 minutes on a wrist-action shaker to ensure equilibrium between phases. For samples requiring minimal thermal equilibration, Dietz and Singley (1979) have ascertained that phase equilibrium is reached in as little as 3 minutes of manual shaking. Therefore, a 15-minute mechanical shaking time should be sufficient. Gas headspace samples of 0.5 ml volume were taken from serum bottles with a syringe for GC analysis.

2. GC Analysis

Headspace samples were analyzed by gas chromatography, using a Varian Aerograph model 1440 GC equipped with a flame-ionization detector. Instrument conditions were: Injector and detector temperatures, approximately 180°C; nitrogen carrier gas and hydrogen flow rates, 30 $ml \cdot min^{-1}$; air flow rate, 300 $ml \cdot min^{-1}$; and column temperature, 100°C (except for analysis of o-dichlorobenzene, which was performed at a column temperature of 150°C).

Two columns were used over the course of these studies. For Henry's constant studies, a 6.1-meter (20-foot) x 3.2 mm (1/8-inch) stainless-steel column packed with 10 percent SP-1000 on 80/100 Supelcoport® (Supelco, Inc.) was used. Retention times for the five primary compounds ranged from 4 to 7 minutes at 100°C; the retention time for o-dichlorobenzene was approximately 15 minutes at 150°C. For all other studies, a 3.05-meter (10-foot) x 3.2 mm (1/8-inch) stainless-steel column packed with 20 percent SP-2100/0.1 percent Carbowax-1500 on 100/120 Supelcoport® (Supelco, Inc.) was used. At 100°C, retention times ranged from 15 seconds for methylene chloride to 3.6 minutes for tetrachloroethylene. Excellent resolution was obtained with both columns, however the latter was superior from the standpoint of required analysis time.

Following analysis, serum bottles were rinsed twice with tap and distilled waters, and oven-dried for at least 2 hours at approximately 150°C to remove any residual volatile organics. Aluminum crimp caps and Teflon® seals were discarded after each use.

C. SATURATED STOCK SOLUTIONS

Organic-saturated aqueous stock solutions were used to add the chemicals in some experiments in order to avoid problems dissolving hydrophobic compounds in the experimental apparatuses. While this means that the initial organic concentrations used in the experiments can only be estimated from available solubility data, this presents no problems since none of the techniques employed in any phase of study requires knowledge of actual aqueous concentrations. Knowledge of relative concentrations suffices.

Stock solutions were prepared with distilled water and the highest purity chemicals commercially available (trichloroethylene, 1,1,1-trichloroethane, chloroform, methylene chloride, and o-dichlorobenzene from Fisher Scientific; tetrachloroethylene from Kodak). The stock solutions consisted of a layer of saturated water floating over a layer of organic. These were kept in 500 ml volumetric flasks to minimize the free surface available for volatilization when the stoppers were removed for sampling. Each flask contained approximately 30 ml of organic, and enough distilled water to rise into the neck of the flask. Samples of saturated solution were always withdrawn from the center of the water layer below the neck of the flask. The saturated stock solutions were occasionally topped with distilled water, and 1 day was allowed for equilibration before use.

D. DILUTION CURVES

Dilution curves, consisting of a series of dilutions of the saturated stock solutions, were made to prove that the headspace chromatography peak heights could legitimately be linearly related to aqueous concentrations of the dilute organics, and that Henry's law was valid throughout the concentration ranges used. These "dilution" curves are not standard curves. They are not used to calculate liquid concentrations from measured gas chromatograph peak heights. In fact, the actual concentrations used in the curves are not -- and need not be -- accurately known. The curves are made only to verify that they are linear.

In these experiments, a series of five dilutions of the stock solutions were added to the 120 ml serum bottles. The total liquid volume was always 25 ml. The bottles were quickly capped and then thermally and phase equilibrated on a wrist-action shaker, prior to analysis of 0.5 ml gas headspace samples on the gas chromatograph. Linear regressions of gas chromatograph peak heights versus dilution fraction show that the response is linear for all compounds studied, and that all lines run through the origin, as expected. The results of these experiments are shown in Table 4. The maximum concentrations used are estimated from available solubility data.

TABLE 4. DILUTION CURVE LINEAR REGRESSIONS

Compound	Max. Conc. (mg/l)	Coefficient of Determination (r^2)
tetrachloroethylene	17	0.998
1,1,1-trichloroethane	18	0.999
trichloroethylene	15	0.998
chloroform	16	0.998
methylene chloride	20	0.999
o-dichlorobenzene	3	1.000

SECTION IV

EQUILIBRIUM STUDIES

A. OBJECTIVES AND PROGRAM OF STUDY

As documented in Section II, Henry's constant is one important parameter affecting performance of air-stripping facilities, via its direct appearance in performance equations [see Equation (8)], and its effect on $K_{\ell}a$ [see Equation (31)]. In this initial phase of study, a large variety of experiments were performed in an attempt to cover types of systems relevant to actual cases of groundwater contamination. These experiments included:

- Henry's constant determinations for each of six compounds in distilled water, over a temperature range of 10 to 30°C, at 5°C intervals.
- Henry's constant determinations for each of six compounds in a solution of 200 mg/l phenol at 25°C. This was an attempt to determine whether the presence of an unstrippable organic compound would affect the apparent Henry's constants of the more volatile componds.
- Henry's constant determinations for each of six compounds in a mixture of the six at two concentration levels at 25°C.
- Henry's constant determinations for each of three compounds in solutions of potassium chloride ranging from 0 to 1 M at 25°C.

These experiments were performed first by batch air stripping. When unexpected and unexplained results were obtained with this method, experiments were reported using a novel technique developed out of this research project: Equilibrium Partitioning in Closed Systems (EPICS). The experiments involving o-dichlorobenzene were not repeated, however, because this compound was difficult to analyze on our gas chromatograph, requiring a higher column temperature than desired for the other five compounds.

B. PROCEDURES

1. Batch Air Stripping

A 1-liter bubble column was used for all batch air stripping Henry's constant determinations. The apparatus is shown in Figure 3. The distance from the air stone to the liquid surface was approximately 51 cm when the column was full. The column was operated isothermally, with the water jacket temperature controlled by a refrigerator/heater circulator (Endocal Model RTE-5, Neslab, Inc.). Gas flow rate was constant during each experiment and measured by a wet test meter. The gas temperature was measured at the wet test meter. The maximum variation in gas temperature, observed during the longest stripping run (35 minutes), was 0.4°C. The air was saturated with water vapor prior to entering the stripping tower to prevent any volume loss by evaporation.

The following basic procedure was used for all stripping experiments. One liter of water, minus the volume of saturated stock solution to be added, was poured into the column. The air was turned on and the flow rate was adjusted to 350 to 390 ml $\cdot$ min^{-1}. The system was allowed approximately 1 hour to reach the correct experimental temperature, and gas flow rate and water and air temperatures were rechecked. The volume of stock solution was then added, and 1 minute was allowed for mixing before sampling began. Using a graduated cylinder, eight 25 ml samples were taken for each Henry's constant determination, at time intervals of 1 to 5 minutes, depending on the compound. Total stripping times, therefore, ranged from 7 to 35 minutes. Samples were immediately poured into 120 ml serum bottles and capped.

The organic concentrations were then analyzed by headspace chromatography, as described in Section III. The serum bottles were allowed to reach ambient temperature, and were then shaken for 10 minutes in a wrist action shaker. Gas headspace samples (0.5 ml) were then withdrawn by syringe (Precision Scientific, Inc.) and injected into the gas chromatograph.

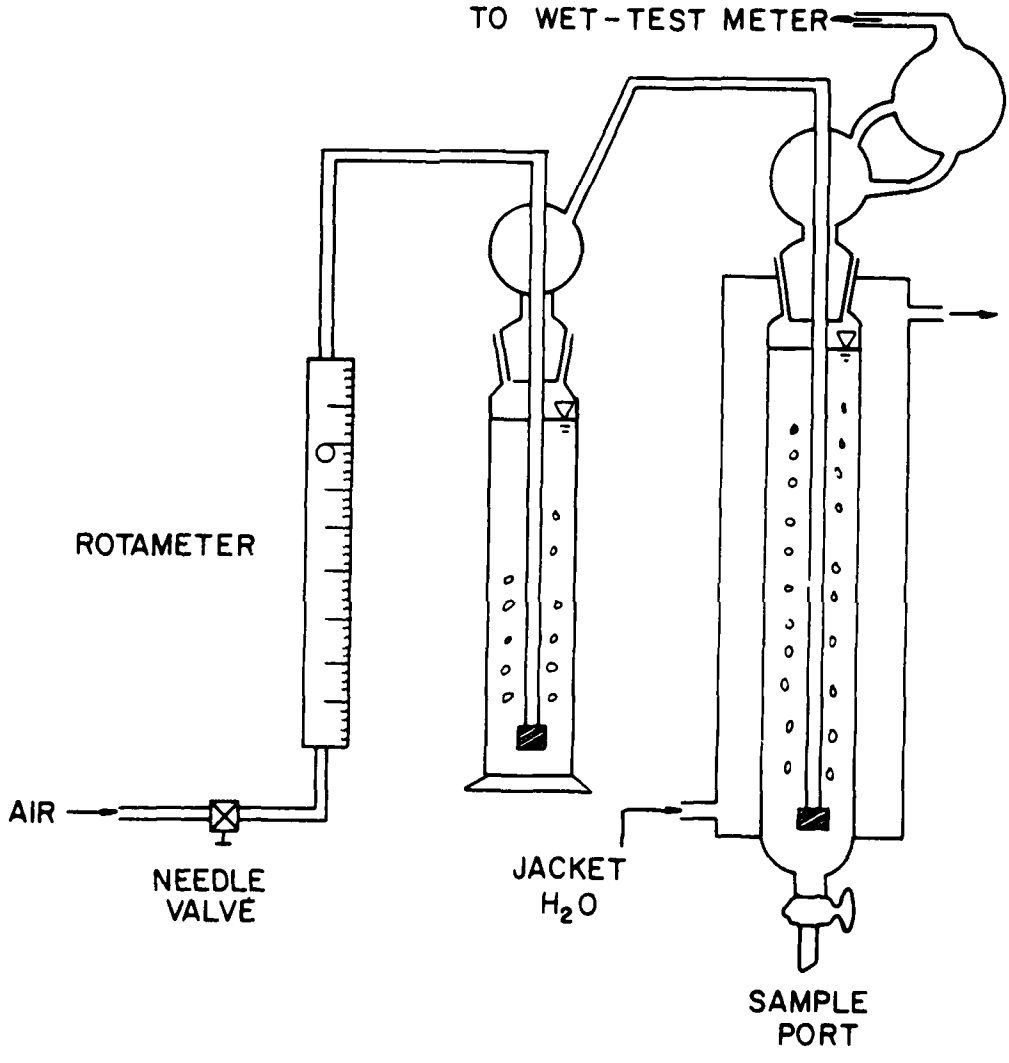

Figure 3. Batch Air-Stripping Apparatus.

Data analysis required a modification of Equation (16) because the sampling process successively decreased the liquid volume of the reactor. The modified form, as derived by Gossett (1983) is:

$$\ell n\ C_{\ell i} = \ell n\ C_{\ell o} - \frac{HG}{RT_g} \sum \frac{\Delta t_i}{V_i} \qquad (86)$$

where:

$C_{\ell i}$ = concentration at the end of the i^{th} time interval ($mol \cdot m^{-3}$);
$C_{\ell o}$ = initial, t=0 reactor concentration ($mol \cdot m^{-3}$);
G = air flow rate measured at T_g ($m^3 \cdot min^{-1}$);
H = Henry's constant ($m^3 \cdot atm \cdot mol^{-1}$);
R = universal gas constant = 8.2056×10^{-5} $m^3 \cdot atm \cdot mol^{-1} \cdot °K^{-1}$;
T_g = temperature at which gas flow is measured (°K);
Δt_i = duration of the i^{th} interval (min);
V_i = reactor volume during the i^{th} time interval (m^3).

A plot of $\ell n\ C_{\ell i}$ vs $\sum \frac{\Delta t_i}{V_i}$ should yield a straight line, with H evaluated from the slope.

a. Temperature-Dependency Experiments

Henry's constants were determined for six compounds at five temperatures ranging from 10 to 30°C, in distilled water. No mixtures were used in the temperature-dependency studies. The volumes of saturated stock solution added to the column depended on the compound studied, and were chosen so that a sufficient concentration of organic remained at the end of the stripping run to allow convenient measurement on the gas chromatograph. Volumes added, and approximate maximum concentrations (calculated from available solubility data) are given in Table 5. The air bubbles in these experiments were visually determined to be roughly 3 mm in diameter, and slightly elliptical.

b. Mixed-Organic Experiment

Henry's constant determinations were made for six compounds in a complex mixture at two concentration levels at 25°C.

TABLE 5. CONCENTRATIONS USED IN BATCH AIR-STRIPPING TEMPERATURE STUDIES

Compound	Volume Saturated Stock Soln. (ml)	Initial Conc. (mg/l)
tetrachloroethylene	20	4
1,1,1-trichloroethane	10	7
trichloroethylene	2	2
chloroform	2	16
methylene chloride	1	20
o-dichlorobenzene	25	3

The concentration levels, termed "high" and "low," differed by a factor of 10. The approximate initial concentrations of each compound in the mixtures of the six are given in Table 6. These concentrations were chosen to give roughly equal readings among the six compounds on the gas chromatograph at the start of the experiment, in order to make data collection as simple as possible. The experiment was run eight times, alternating between the high and low concentration levels, giving four Henry's constant measurements for each compound at each concentration level.

The stock solutions were kept in a water bath at 25°C for these experiments because the volumes of organic-saturated solutions added to the column were appreciable, and could have affected the system temperature. For the high-concentration experiments, a total of 275 ml of saturated stock solutions were added to the column. It was apparent from direct observation of the bubbles in the column that this concentration level caused a slight decrease in air bubble size, compared to that found in the temperature-dependency experiments.

The analysis of o-dichlorobenzene on the gas chromatograph presented some difficulty because of its long retention time. Analyses of the other five compounds were done initially at a column temperature of 100°C. The column temperature was then raised to 150°C for the analysis of o-dichlorobenzene. This required a second 0.5 ml gas headspace sample to be taken from the serum bottles containing the samples taken at 0, 5, and 10 minutes. Since the headspace samples are small compared to the total gas headspace volume, the error caused by taking a second sample is insignificant compared to other experimental errors.

Before the mixed-organic experiment was performed, it had to be demonstrated that Henry's law was valid in the high-concentration ranges for single component systems. Henry's constants at 25°C were measured for trichloroethylene in distilled water at two concentration levels, and for chloroform at two concentration levels. The results of these experiments are listed in Table 7. If results for both concentrations are grouped as a single class, the

TABLE 6. ORGANIC CONCENTRATIONS IN BATCH AIR-STRIPPING MIXTURE STUDIES

Compound	Low Conc. Mixture (mg/l)	High Conc. Mixture (mg/l)
tetrachloroethylene	2	20
1,1,1-trichloroethane	4	40
trichloroethylene	5	50
chloroform	16	160
methylene chloride	10	100
o-dichlorobenzene	0.5	5
total organic conc.	37.5	375

TABLE 7. HENRY'S CONSTANT IN HIGH-CONCENTRATION SINGLE-COMPONENT SYSTEMS AT 25°C

Compound	Concentration (mg/l)	Henry's Constant (m^3-atm/mol)
trichloroethylene	2	0.00992
	50	0.0103
chloroform	4	0.00424
	80	0.00428

coefficients of variation are 2.7 percent and 0.6 percent for trichloroethylene and chloroform, respectively -- this is less than the typical experimental error in Henry's constant measurement (see Figure 13). Therefore, changes in Henry's constants measured in the batch air-stripping mixture studies cannot be ascribed to the use of concentrations outside the range obeying Henry's law.

c. Phenol Experiments

Experiments using a solution of 200 mg/l phenol instead of distilled water were performed to determine whether the presence of another organic, at a low concentration, could affect Henry's constants measured in a stripping tower. Phenol is nonvolatile, compared to the other six organic compounds used in this experiment, and its concentration did not change measurably over the short period of air stripping. Henry's constants were measured separately for the six compounds in the presence of phenol at 25°C. The volumes of saturated stock solutions added to the column in these experiments, and the approximate initial concentrations, are shown in Table 8. The phenol concentration caused a significant decrease in the air bubble size. The average bubble in these experiments was spherical and roughly 1 mm in diameter.

d. Ionic Strength Experiments

Henry's constant determinations were made for tetrachloroethylene, chloroform, and methylene chloride in solutions of 0.3, 0.6, and 1 M potassium chloride at 25°C. The concentrations of the three chemicals used in these experiments were approximately the same as those shown in Table 8. The bubble size decreased in these experiments with increasing ionic strength. At 1 M KCl, the average bubble was spherical with a diameter of roughly 1 mm.

2. Equilibirum Partitioning in Closed Systems

The measurement of Henry's constant by EPICS depends on the assumption that equilibirum between the gas and liquid phases in the serum bottles has been reached prior to measurement of the gas-phase concentrations. An experiment was performed in order to find out how long it takes to reach equilibrium.

TABLE 8. CONCENTRATIONS USED IN BATCH AIR-STRIPPING PHENOL EXPERIMENTS

Compound	Volume Saturated Stock Soln. (ml)	Initial Conc. (mg/l)
tetrachloroethylene	10	2
1,1,1-trichloroethane	5	4
trichloroethylene	5	5
chloroform	2	16
methylene chloride	0.5	10
o-dichlorobenzene	5	0.5

Dietz and Singley (1979), in their discussion of headspace chromatography, reported that compounds with high Henry's constants took longer to reach equilibrium. Preliminary experiments confirmed this finding, and also showed that serum bottles containing large liquid volumes also took longer to reach equilibrium. Therefore, the final experiment was performed using a high liquid volume, and a compound with a high Henry's constant, in order to ensure that equilibrium would be reached in all systems. 0.1 ml aliquots of 1,1,1-trichloroethane-saturated water were added to eight serum bottles containing 100 ml of distilled water. The bottles were placed in an insulated chest at 25°C, and the resulting gas concentrations were measured at times ranging from 15 minutes to 8 days. The results of this experiment, shown in Figure 4, indicate that even under these adverse conditions, the headspace concentration at 4 hours, and thus the fraction of equilibrium achieved in the serum bottle at that time, was within 2 percent of the value measured at 8 days. Therefore, equilibrium is essentially complete within 4 hours.

a. Temperature-Dependency Experiments

Six 120 ml serum bottles were used for each Henry's constant determination by EPICS. Glass volumetric pipets were used to fill three of the bottles with 100 $\pm$ 0.08 ml of distilled water, and three with 10 $\pm$ 0.01 ml. These six bottles provided a total of nine pairs of high and low liquid volume closed systems from which Henry's constants were calculated.

A small sample of saturated stock solution was added to each serum bottle (alternating between high and low volume bottles) which was then promptly sealed with a Teflon® -lined rubber septum and an aluminum crimp cap (Supelco, Inc.). These volumes, the resulting total liquid volumes, and the approximate initial liquid concentrations for each chemical are given in Table 9.

The aliquots of stock solution were withdrawn from the volumetric flasks using microliter syringes (Hamilton, Inc.). Samples were taken from the center of the water layer in the flask, and then injected below the liquid surface in the serum bottles in order to minimize mass loss prior to sealing the bottles. The samples of stock

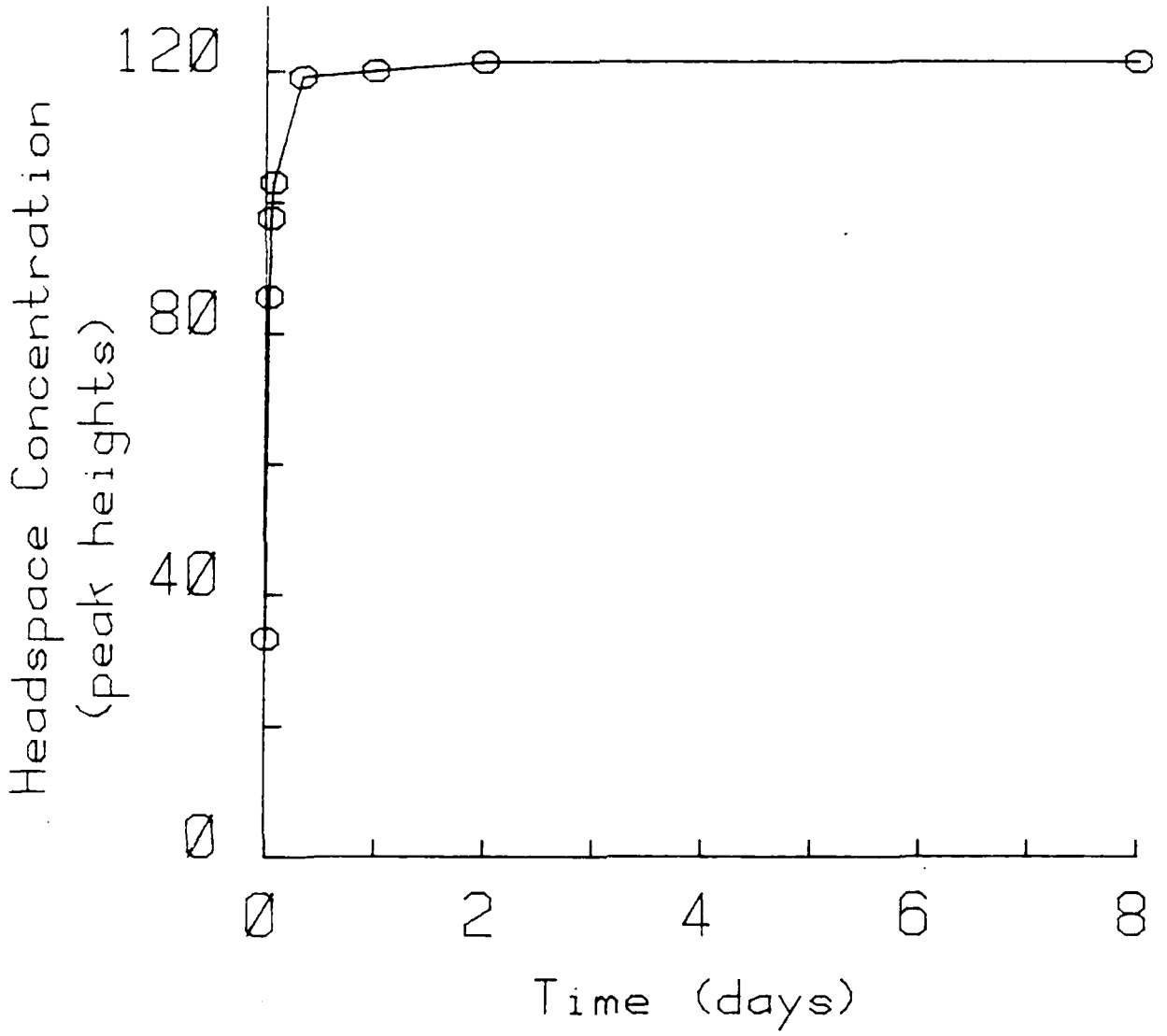

Figure 4. Equilibration in EPICS Serum Bottles (1,1,1-trichloroethane).

TABLE 9. SATURATED STOCK SOLUTION ADDITIONS TO EPICS SERUM BOTTLES

Compound	Saturated Stock Solution Added (µl)	System 1 Volume, (ml)	System 1 Conc. (mg/l)	System 2 Volume, (ml)	System 2 Conc. (mg/l)
tetrachloroethylene	1000	11.0	20	101.0	2
1,1,1-trichloroethane	500	10.5	40	100.5	4
trichloroethylene	500	10.5	50	100.5	5
chloroform	200	10.2	160	100.2	16
methylene chloride	50	10.05	100	100.05	10

solution were not injected through the septums because it was feared that piercing the Teflon® liner might allow the rubber to absorb some of the organic added.

The serum bottles were then placed in an insulated chest. The bottles stood in water held at the desired temperature by a refrigerator/heater circulator (Endocal Model RTE-5, Neslab, Inc.). The water temperature was measured by a mercury thermometer graduated in 0.1°C, and was never observed to fluctuate. The serum bottles were allowed 24 hours to reach equilibrium. While the work of Dietz and Singley (1979) and the authors' own experiments indicate that 24 hours is far longer than necessary, it provides a large margin of safety and is experimentally convenient. The bottles were removed from the chest three times during this period, and shaken by hand for approximately 40 seconds. The final shaking took place more than 2 hours prior to measurement of the equilibrium gas phase concentrations on the gas chromatograph, to ensure that the removal for shaking could not affect the temperature of the serum bottles.

Henry's constants were calculated according to Equation (20) from the gas chromatograph peak heights and the total liquid volumes given in Table 9. The six serum bottles gave a total of nine high and low liquid volume pairs from which to calculate Henry's constant. The average of these nine values is reported as Henry's constant.

b. Phenol Experiments

The effect of 200 mg/l phenol on the Henry's constants of four compounds was studied using a simple comparison of equilibrium gas concentrations. In these experiments, pairs of bottles were set up with identical liquid volumes (90 ml). Half of the bottles contained a solution of 200 mg/l phenol, and half contained distilled water. All bottles were then spiked with the same mass of volatile organic and allowed to reach equilibrium prior to measurement of their gas-phase concentrations. The masses added, and initial liquid concentrations were approximately equal to those shown in Table 9 for "System 2."

c. Mixed-Organic Experiment

In this experiment, the equilibrium gas-phase concentrations of each of the volatile organics in mixtures of the six, at two concentration levels, were compared with the equilibrium gas concentrations of each compound alone in distilled water.

The initial concentrations of organics in the mixtures were the same as those used in the batch air-stripping mixed-organic experiment (Table 6). One liter of the mixture at the "high" concentration level (375 mg/l total organic concentration) was prepared by adding appropriate volumes of saturated stock solutions and distilled water to a volumetric flask.

The EPICS serum bottles used in this experiment all contained 100 ml of liquid. The high-concentration mixture bottles contained 100 ml of the mixture described above. The low-concentration bottles were prepared by adding 10 ml of the mixture to 90 ml of distilled water. Five bottles were prepared at each concentration level.

The reference systems, containing each compound alone in distilled water, were prepared at the high-concentration level only. Six reference serum bottles were prepared for each compound. The bottles were filled with 100 ml of distilled water, a small volume was withdrawn, and then the bottles were spiked with that volume of saturated stock solution. This procedure was basically the same as that used in the temperature-dependency experiments, except that the total volume of all bottles was exactly 100 ml. The volumes of stock solutions added, and the approximate initial concentrations are the same those shown for "System 2" in Table 9.

It was not necessary to prepare reference systems at the low concentration level since the difference between the two levels was known. If there were no changes in Henry's constant caused by the mixtures, the equilibrium gas-phase concentrations in the high-concentration mixture bottles would be the same as those in the reference bottles, and the gas concentrations in the low-concentration mixture bottles would be exactly one-tenth as great.

o-Dichlorobenzene was present in the mixtures so that this experiment could be legitimately compared to the batch air-stripping mixed-organic experiment. However, the equilibrium gas-phase concentrations of o-dichlorobenzene were not measured in these experiments, and no reference systems were prepared for it, since it was difficult to analyze on the gas chromatograph and the batch air-stripping results showed no significant effect of mixtures on its Henry's constant.

d. Ionic Strength Experiments

The changes in the effective Henry's constants of tetrachloroethylene, chloroform, and methylene chloride due to increasing system ionic stength were analyzed, using the modified EPICS procedure outlined in Section II. C.

All serum bottles used in these experiments contained 90 ml of liquid. Three reference systems, containing distilled water, and five systems containing a range of salt solutions (0-1 M, KCl), were prepared for each chemical. All systems were spiked with the same volume of saturated stock solution for each compound tested. The bottles were then capped and allowed to reach equilibrium at 25°C before measurement of the gas-phase organic concentrations.

Activity coefficients were calculated according to Equation (22). C_g, the reference gas concentration, was taken as the average of the concentrations measured in the three reference systems.

C. RESULTS

1. The Temperature Dependence of Henry's Constant

The results from both batch air-stripping and EPICS experiments demonstrate the significant temperature dependency of Henry's constants. Henry's constants measured by EPICS, however, tended to be higher than those measured by batch air stripping. These differences increased at higher temperatures. The maximum difference between results obtained by the two techniques was 21 percent, for trichloroethylene at 30°C. Only the results for 1,1,1-trichloroethane showed no differences between the two techniques.

Linear regressions of the natural log of Henry's constant versus reciprocal absolute temperature [Equation (11)] were made using the results of both techniques. Temperature-dependence equations derived from these regressions, as well as the regression coefficients of determination (r^2), are listed in Tables 10 and 11.

Since the coefficients of determination are all near one, it is clear that the results fit the model given by Equation (11), and that the heats of dissolution (ΔH_o) of these compounds are all nearly constant over the temperature range of 10 - 30°C. Calculated values of ΔH_o, however, would be higher, using the EPICS data for tetrachloroethylene, and slightly lower for chloroform and methylene chloride.

Plots of Henry's constant versus temperature were made, using the temperature regression equations listed in Tables 10 and 11. These plots are shown in Figures 5 through 9.

2. Results of the Mixed Organic Experiments

The results of the mixed organic experiment using EPICS were partially inconclusive. The equilibrium gas-phase concentrations (expressed in gas chromatograph peak height units) and standard deviations of the single component, and high- and low-concentration mixture systems are shown in Table 12.

The results show that the measured equilibrium gas-phase concentrations in the distilled water reference systems and in the mixtures were approximately equal. One should not give too much weight to this comparison, however, because of the different techniques used to add the chemicals to these systems. For this experiment to be accurate, identical masses of the volatile compounds must have been added to the reference and high concentration mixture systems. In the reference systems, microliter samples were taken from the stock solution bottles and added directly to the serum bottles. In the mixtures, volumes of stock solution were taken in glass pipets and added to a volumetric flask to make 1 liter of mixture. Dilutions of this mixture were then taken by pipet and added to the serum bottles. Possible sources of error include failure to measure exact volumes in the microliter syringes, and volatilization of the organics

TABLE 10. HENRY'S CONSTANT TEMPERATURE DEPENDENCIES DETERMINED BY EPICS

Compound	Henry's Constant at 20°C (m^3-atm/mol)	Temperature Dependence Regression Equation (T, °K)	r^2
tetrachloroethylene	0.0130	H=exp(13.12-5119/T)	0.995
1,1,1-trichloroethane	0.0132	H=exp(10.21-4262/T)	0.998
trichloroethylene	0.00764	H=exp(11.94-4929/T)	0.992
chloroform	0.00333	H=exp(8.553-4180/T)	0.988
methylene chloride	0.00225	H=exp(8.200-4191/T)	0.989

TABLE 11. HENRY'S CONSTANT TEMPERATURE DEPENDENCIES DETERMINED BY BATCH AIR STRIPPING

Compound	Henry's Constant at 20°C (m^3-atm/mol)	Temperature Dependence Regression Equation (T, °K)	r^2
tetrachloroethylene	0.0116	H=exp(11.32-4622/T)	0.999
1,1,1-trichloroethane	0.0134	H=exp(9.975-4186/T)	0.998
trichloroethylene	0.00674	H=exp(9.703-4308/T)	0.980
chloroform	0.00304	H=exp(8.956-4322/T)	0.995
methylene chloride	0.00197	H=exp(9.035-4472/T)	0.989
o-dichlorobenzene	0.00113	H=exp(15.96-6665/T)	0.973

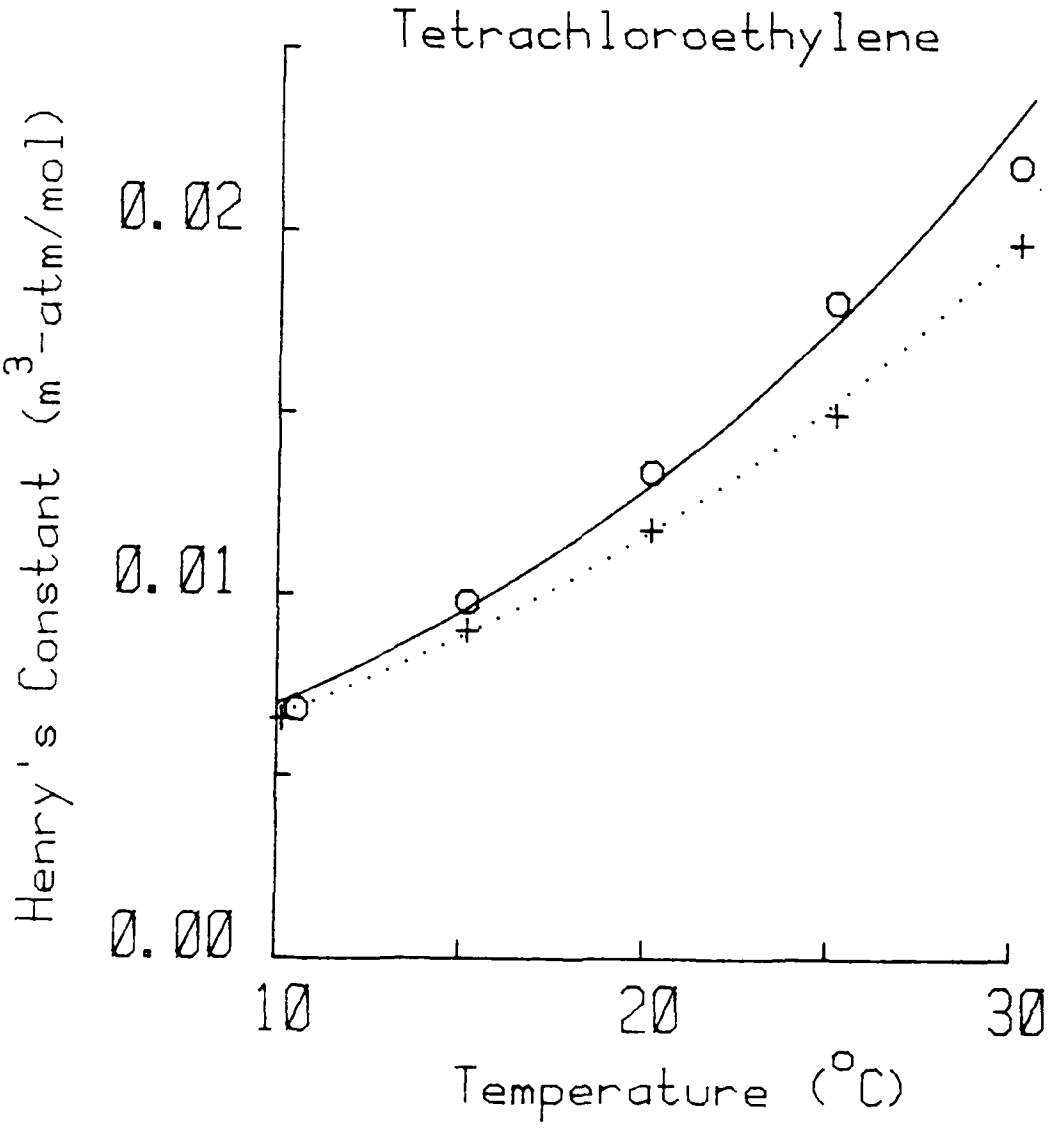

Figure 5. The Temperature Dependence of Henry's Constant for Tetrachloroethylene.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

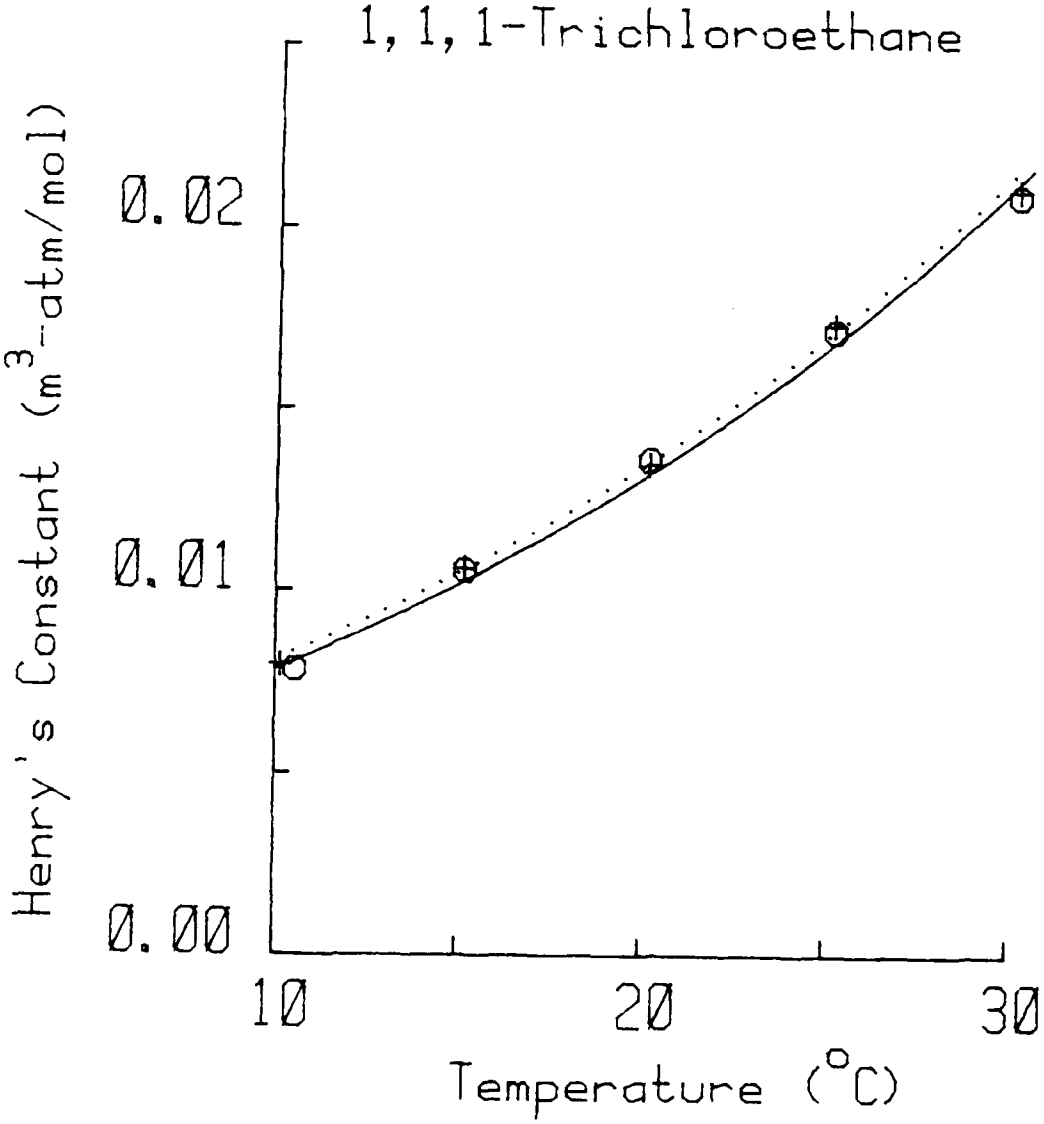

Figure 6. The Temperature Dependence of Henry's Constant for 1,1,1-Trichloroethane.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

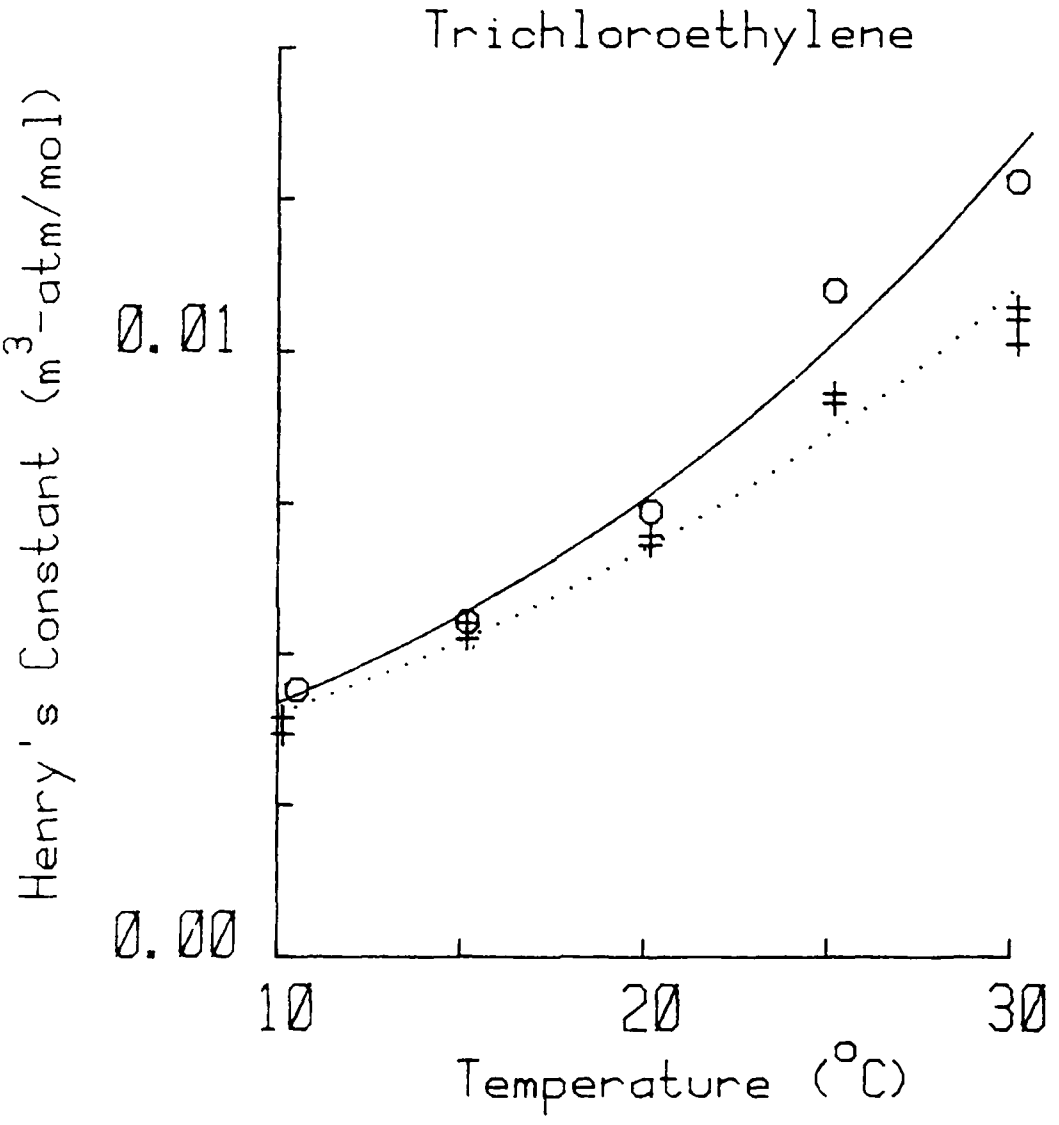

Figure 7. The Temperature Dependence of Henry's Constant for Trichloroethylene.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

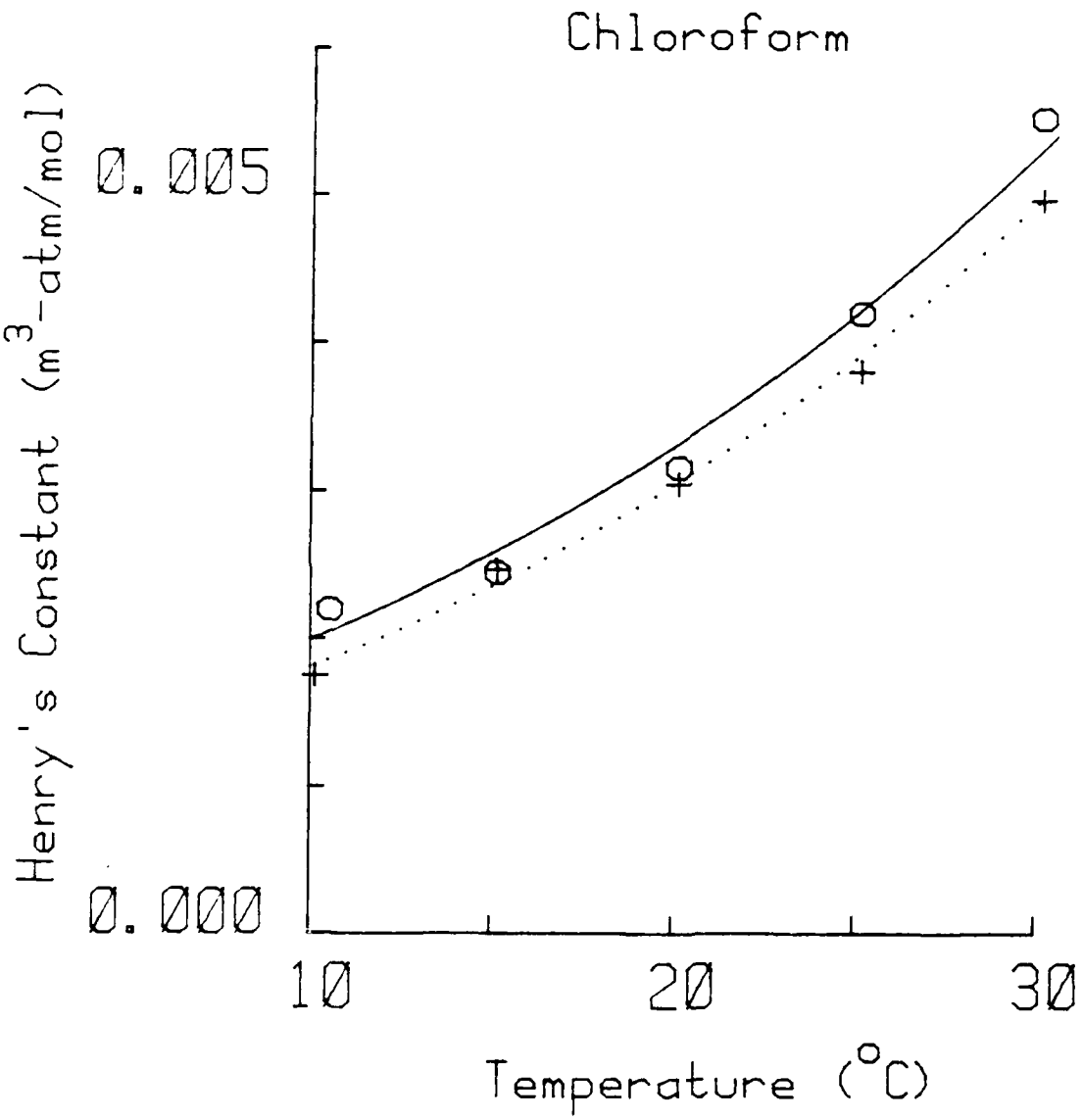

Figure 8. The Temperature Dependence of Henry's Constant for Chloroform.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

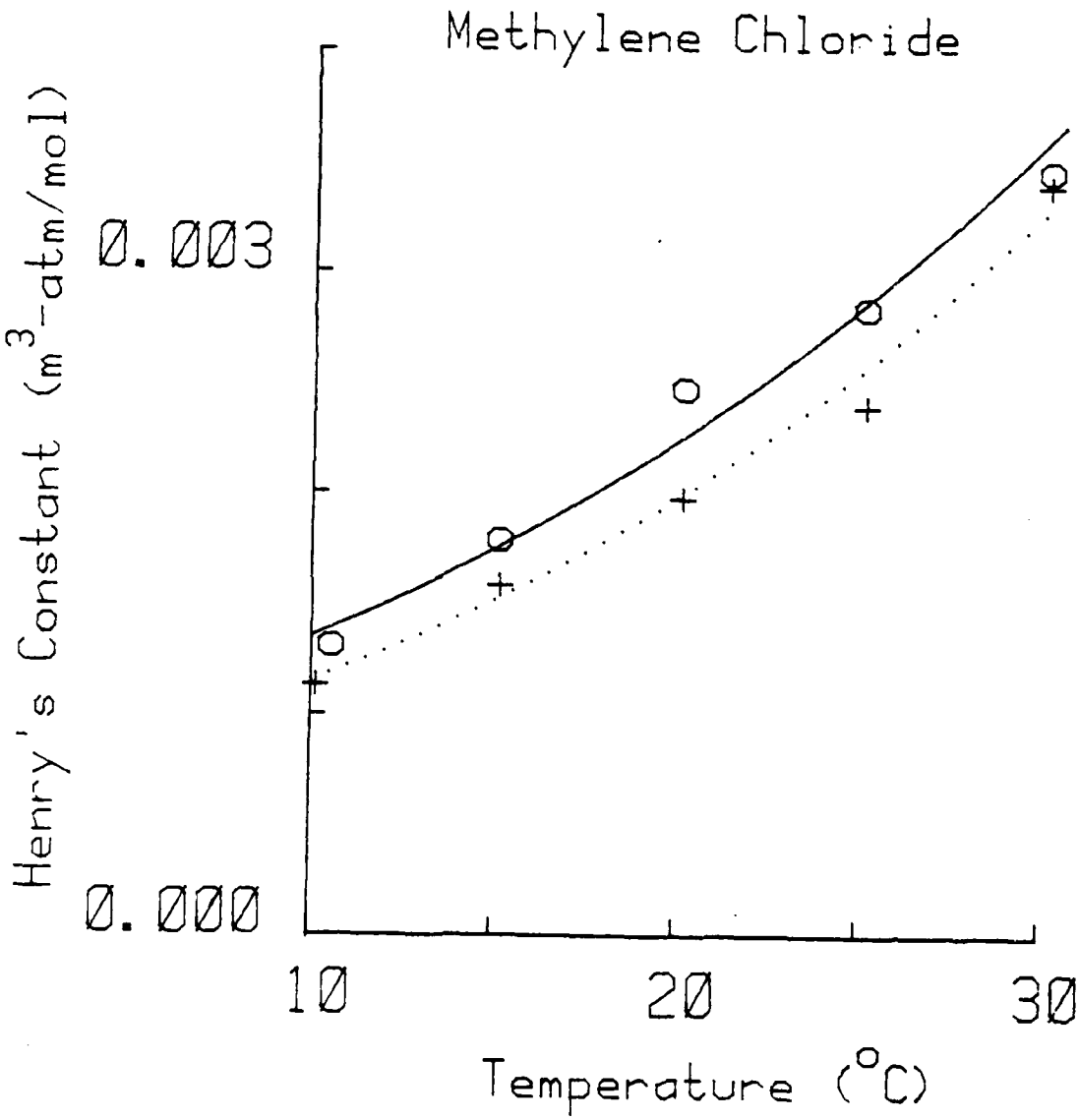

Figure 9. The Temperature Dependence of Henry's Constant for Methylene Chloride.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

TABLE 12. RESULTS OF EPICS MIXED ORGANIC EXPERIMENT

Compound	Equilibrium Gas Concentrations (peak height units) Pure Water	'Low' Mixture	'High' Mixture
		(x 10)	
tetrachloroethylene	56.0 ± 1.8	58.1 ± 0.6	59.0 ± 0.4
1,1,1-trichloroethane	86.0 ± 0.8	79.5 ± 2.0	79.3 ± 3.1
trichloroethylene	61.0 ± 1.5	54.7 ± 1.1	56.7 ± 2.6
chloroform	50.3 ± 1.0	54.2 ± 1.5	54.6 ± 2.2
methylene chloride	54.9 ± 2.6	53.8 ± 1.1	54.7 ± 2.1

TABLE 13. RESULTS FROM *MIXED ORGANIC STUDIES* USING BATCH AIR STRIPPING

Compound	Measured Henry's Constants at 25°C (m^3-atm/mol) Low Conc. Mixture Mean	Low Conc. Mixture Coeff. of Variation	High Conc. Mixture Mean	High Conc. Mixture Coeff. of Variation
tetrachloroethylene	0.0172	1%	0.0211	2%
1,1,1-trichloroethane	0.0177	2%	0.0210	1%
trichloroethylene	0.0115	2%	0.0122	2%
chloroform	0.00442	3%	0.00451	2%
methylene chloride	0.00243	5%	0.00252	5%
o-dichlorobenzene	0.00176	6%	0.00167	5%

from the six-component mixture during its preparation. Therefore, results such as the apparent decrease in the gas concentration of 1,1,1-trichloroethane between the reference systems and the mixtures, should be seen as evidence of experimental error rather than evidence of a decrease in Henry's constant.

The results for the high- and low-concentration mixtures, however, can be legitimately compared. They show no differences, outside the standard deviations of the measurements, in partitioning in these systems. This proves that the Henry's constant of each chemical was the same in both mixtures.

To summarize, the results of the EPICS mixed organic experiment do not give conclusive evidence that the Henry's constants in the reference systems and in the mixtures were the same, but they do show that the Henry's constants were the same in the high- and low-concentration mixtures. This is an important result, because it proves that the results of the batch air-stripping mixed organic experiment, given below, must be in error.

The results of the six-component mixture experiments using batch air stripping show significant (> 10 percent) increases over the values obtained in distilled water for two compounds in the low concentration mixture, and for four compounds in the high concentration mixture. The four replicates done at each of the concentration levels indicate very good precision. The results, showing the Henry's constant measurements and coefficients of variation are given in Table 13. These results are compared to the Henry's constants measured by batch air stripping in distilled water in Table 14.

3. The Effect of 200 mg/l Phenol on Henry's Constant

Comparison of the equilibrium gas-phase concentrations of volatile organics using the EPICS procedure at 25°C showed no significant differences between bottles containing distilled water and bottles containing a solution of 200 mg/l phenol for any of the four compounds tested. This proves that 200 mg/l phenol cannot affect the Henry's constants of these compounds. The results of these experiments with average equilibrium gas-phase concentration

TABLE 14. RESULTS FROM BATCH AIR STRIPPING--MIXED ORGANIC STUDIES

Compound	Measured Henry's Constants at 25°C (m^3-atm/mol) Pure Water	'Low' Mixture Mean	'Low' Mixture Change From Pure Water	'High' Mixture Mean	'High' Mixture Change From Pure Water
tetrachloroethylene	0.0149	0.0172	+ 15%	0.0211	+ 42%
1,1,1-trichloroethane	0.0173	0.0177	+ 2%	0.0210	+ 21%
trichloroethylene	0.0101	0.0115	+ 14%	0.0122	+ 21%
chloroform	0.00411	0.00442	+ 8%	0.00451	+ 10%
methylene chloride	0.00239	0.00243	+ 2%	0.00252	+ 5%
o-dichlorobenzene	0.00164	0.00176	+ 7%	0.00167	+ 2%

expressed in gas chromatograph peak height units, are given in Table 15.

Henry's constant determinations by batch air stripping in 200 mg/l phenol at 25°C showed significant (> 10 percent) increases over the values obtained in distilled water for all six compounds tested. These results, and the values measured in distilled water, are shown in Table 16. The coefficients of determination (r^2) of the linear regressions of Equation (86) for these experiments were all greater than 0.99, an indication of good precision.

4. The Effect of Ionic Strength on Apparent Henry's Constants

The results of the ionic strength experiments using both EPICS and batch air stripping are plotted in Figures 10 through 12. The log of apparent Henry's constant is plotted against ionic strength to show agreement with the empirical model given by Equation (15). All data are reasonably linear, and fit the model quite well, except for those obtained by batch air stripping for tetrachloroethylene.

The lowest coefficient of determination (r^2) for the linear regressions of the EPICS results was 0.91, for methylene chloride. Empirical "salting-out" coefficients, determined from the slopes of these plots, are listed in Table 17, and are on the order of 0.1, as predicted by Butler (1964). The value listed for tetrachloroethylene, as determined by batch air stripping, is calculated from the initial linear part of that curve.

The EPICS results show that significant (> 10 percent) increases in Henry's constants do not occur, for any of the compounds, until the ionic strength of the system is greater than 0.26. The batch air stripping results show a significant increase in the Henry's constant of tetrachloroethylene when the ionic strength is greater than 0.074 M.

5. The Precision of Henry's Constant Measurements

The six high and low liquid volume serum bottles used for each EPICS Henry's constant determination gave nine pairs of equilibrium gas concentrations for substitution into Equation (20). Henry's

TABLE 15. RESULTS FROM PHENOL STUDIES USING EPICS

Compound	Equilibrium Gas Concentrations (peak height units) In Distilled Water	In 200 mg/l Phenol
tetrachloroethylene	35.7	37.5
trichloroethylene	92.3	92.6
chloroform	55.5	55.0
methylene chloride	62.2	61.9

TABLE 16. RESULTS FROM PHENOL STUDIES USING BATCH AIR STRIPPING

Compound	Measured Henry's Constants at 25°C (m^3-atm/mol) Distilled Water	200 mg/l Phenol	% Change
tetrachloroethylene	0.0149	0.0195	+ 31%
1,1,1-trichloroethane	0.0173	0.0208	+ 20%
trichloroethylene	0.0101	0.0131	+ 30%
chloroform	0.00411	0.00464	+ 13%
methylene chloride	0.00239	0.00266	+ 11%
o-dichlorobenzene	0.00164	0.00187	+ 14%

TABLE 17. RESULTS OF IONIC STRENGTH STUDIES

Compound	Empirical "Salting-out" Coefficients Batch Air Stripping	EPICS
tetrachloroethylene	0.56	0.20
chloroform	0.15	0.13
methylene chloride	0.21	0.12

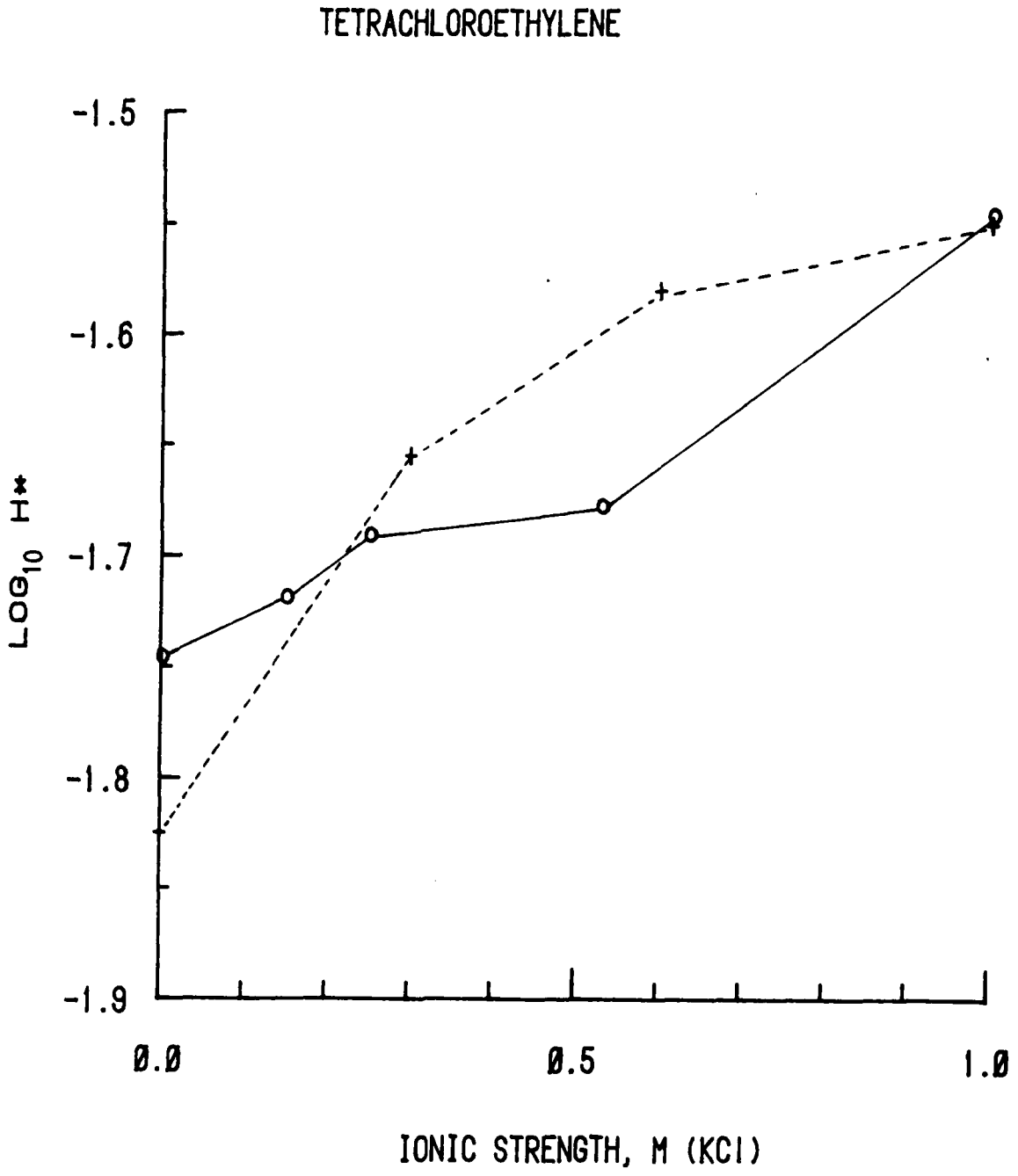

Figure 10. The Effect of Ionic Strength on the Apparent Henry's Constant of Tetrachloroethylene at 25°C.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

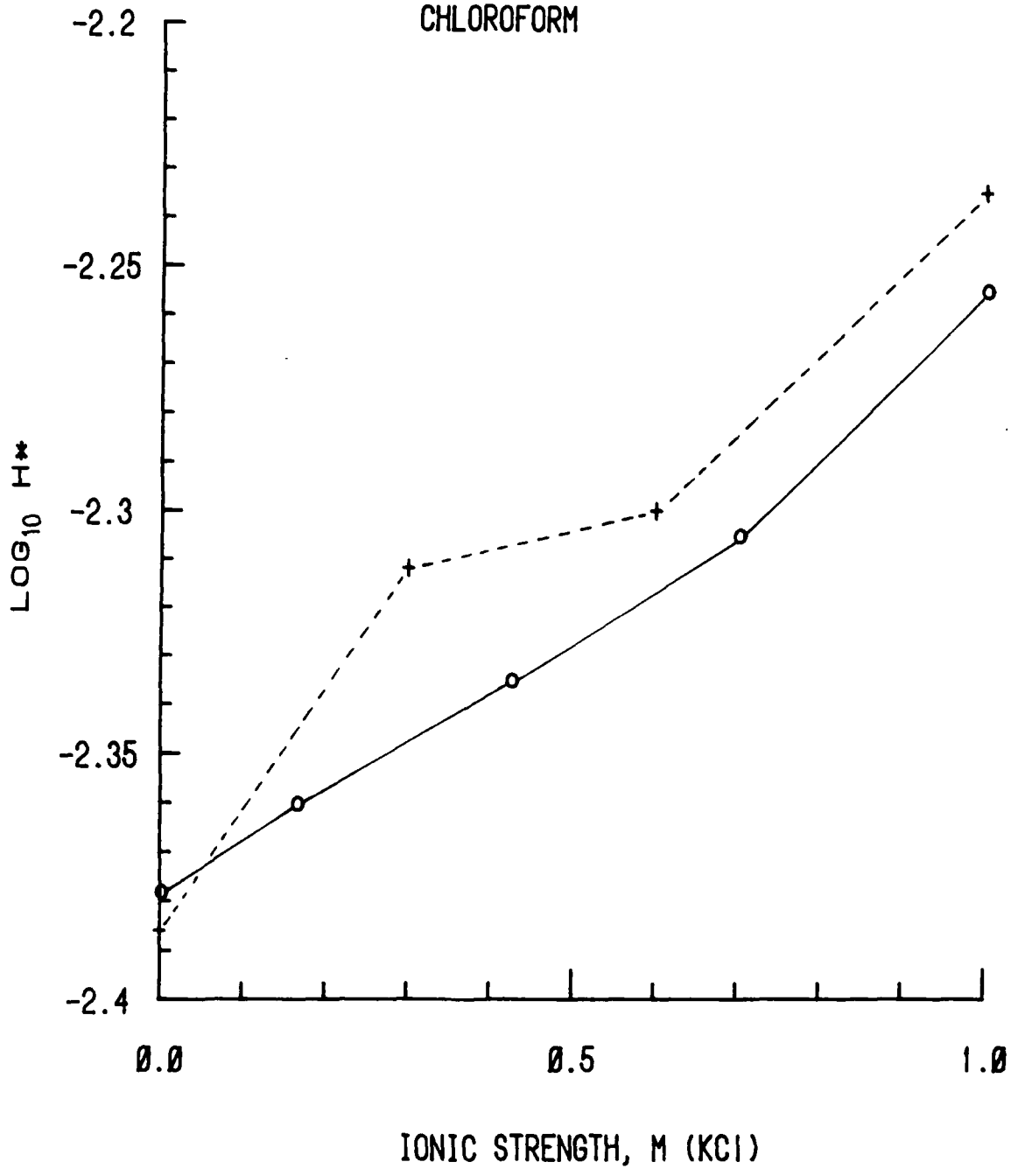

Figure 11. The Effect of Ionic Strength on the Apparent Henry's Constant of Chloroform at 25°C.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

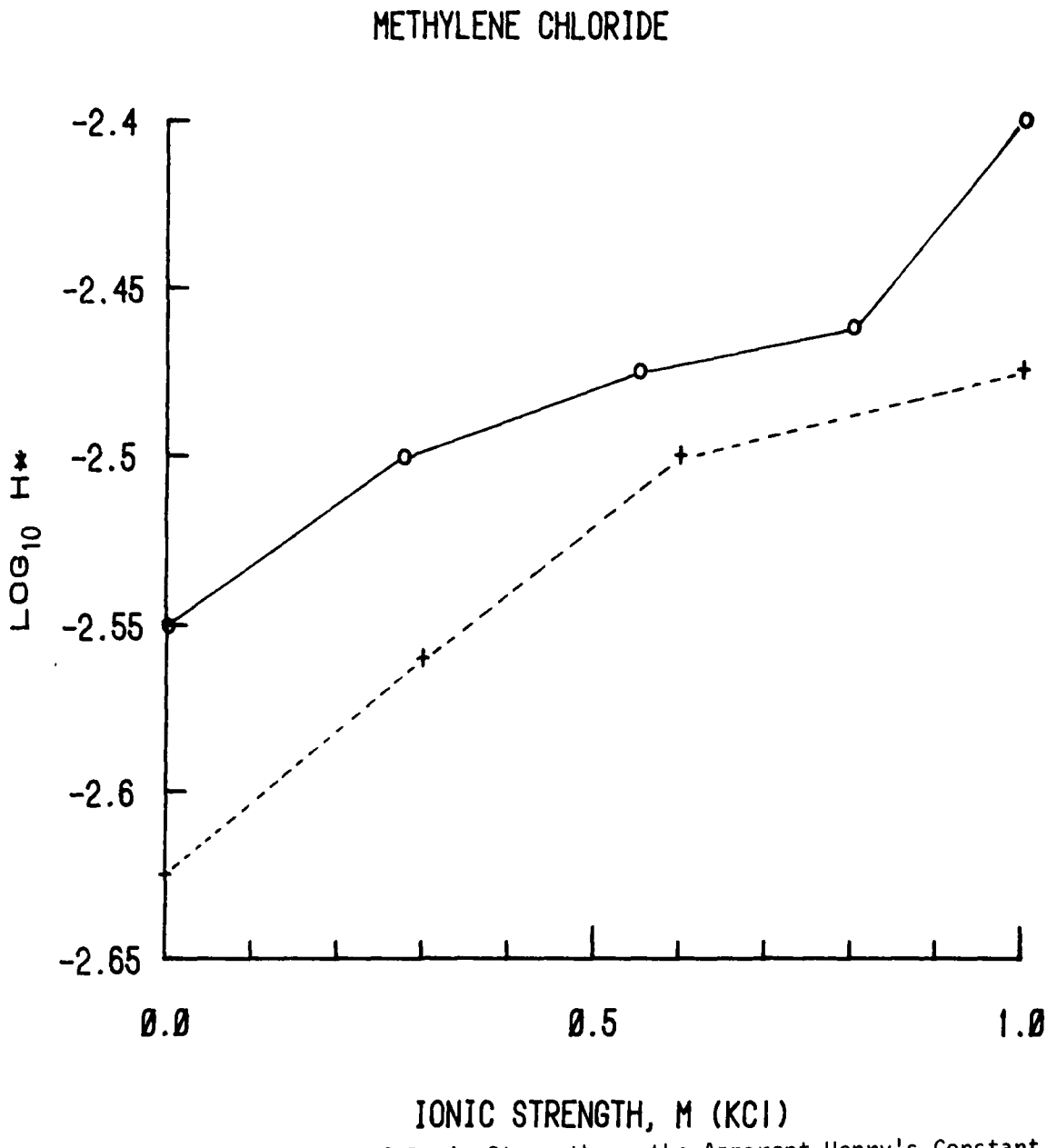

Figure 12. The Effect of Ionic Strength on the Apparent Henry's Constant of Methylene Chloride at 25°C.

EPICS results are indicated by solid lines and circles. Batch air-stripping results are indicated by dotted lines and plusses.

constant was taken as the average of these nine calculations. For the 25 Henry's constants measured by EPICS for compounds in distilled water (5 compounds at 5 temperatures), the average coefficient of variation (standard deviation/mean) of the nine Henry's constant calculations was less than 5 percent. A plot of coefficient of variation versus Henry's constant for these 25 measurements is shown in Figure 13. The plot shows no trends, indicating that EPICS measurements have approximately 5 percent precision for any compound within this range of volatilities.

The best measure of the precision of the batch air-stripping Henry's constant determinations is the reproducibility of the results of the mixed organic experiments. Henry's constant measurements were repeated for six compounds, four times at the "low" concentration level, and four times at the "high" concentration level. The average coefficient of variation for these 48 Henry's constant measurements was less than 5 percent.

Another measure of the precision of batch air-stripping measurements are the coefficients of determination (r^2) of the linear regression of Equation (86) used for each Henry's constant measurement. For the 30 measurements made for compounds in distilled water (6 compounds at 5 temperatures), r^2 was always greater than 0.98.

D. DISCUSSION

Based on the experimental procedures and theoretical background sections, the Equilibrium Partitioning in Closed Systems technique is much simpler than batch air stripping. EPICS' Henry's constant determinations are performed in serum bottles, while batch air stripping requires construction of a stripping column with a constant, measured gas flow. In addition, it is difficult to prove that the main theoretical assumptions required by batch air stripping (complete equilibrium and mixing) are valid.

More importantly, discrepancies between the results obtained by the two techniques indicate that EPICS is a more accurate method for determining the Henry's constants of volatile compounds. The fact that the EPICS results were all greater than or equal to the batch air

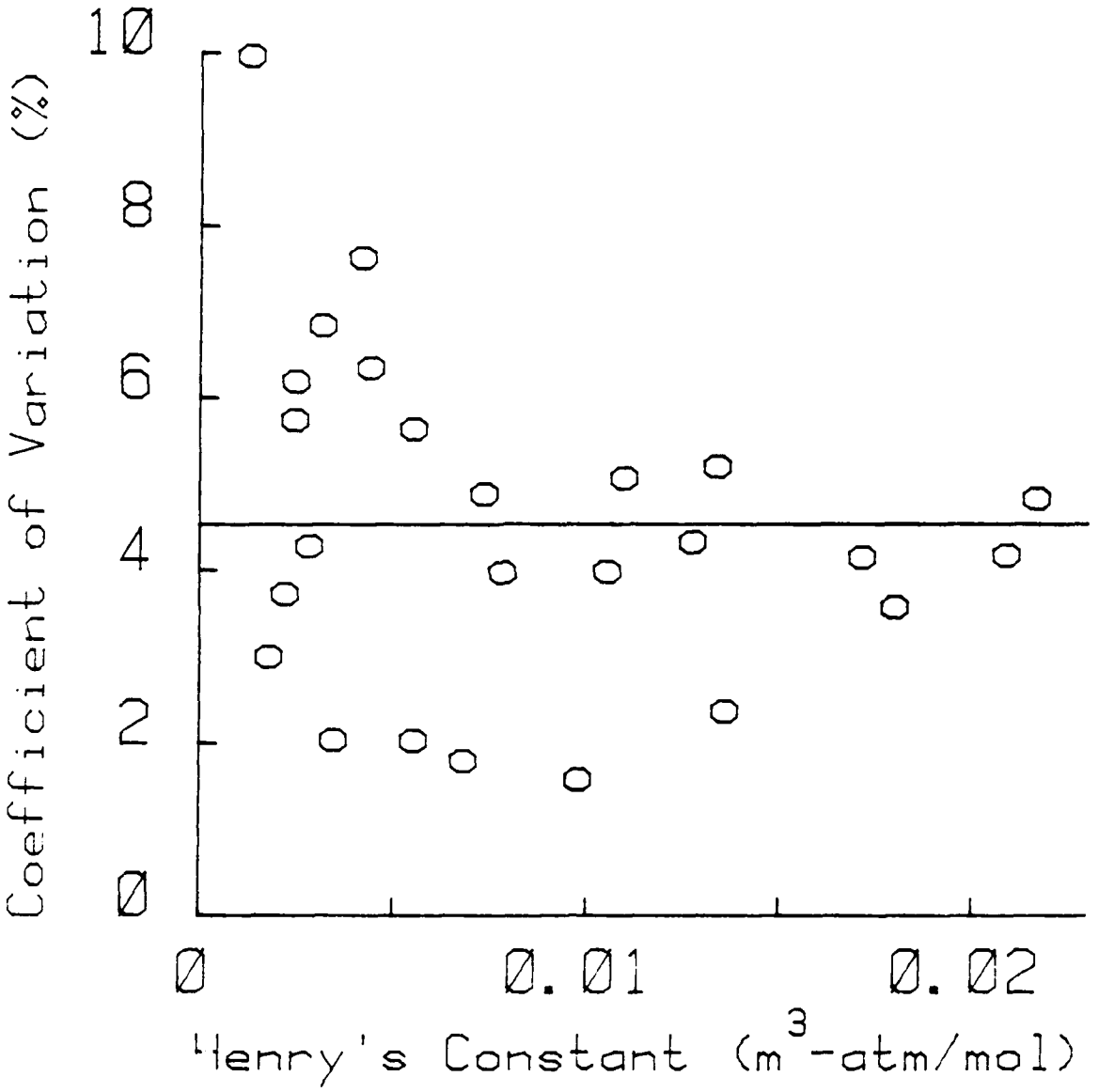

Figure 13. Coefficient of Variation Versus Henry's Constant for EPICS Measurements.

stripping results implies that there is a systematic error in the bubble column method due to lack of equilibrium. Additionally, the results of the phenol and mixture studies suggest that there may be deficiencies in the theoretical derivation of the batch air-stripping technique. One conclusion of these studies is that the common research practice of measuring Henry's constants of chemicals in mixtures by batch air stripping is probably ill-advised.

1. Temperature-Dependence Studies

The temperature-dependency equations determined by EPICS (Table 10) should be used to calculate Henry's constants. The differences between the values of Henry's constants measured by EPICS and batch air stripping between 10 and 30°C in distilled water are not great, but they do indicate that one cannot be sure of batch air-stripping results for volatile compounds. There were no significant differences between results for 1,1,1-trichloroethane; and for chloroform and methylene chloride, the EPICS results are only about 10 percent higher. For tetrachloroethylene and trichloroethylene, the differences are greater (up to 21 percent).

The model of approach to equilibrium in batch air-stripping towers suggests a likely explanation for the differences in results obtained by the two techniques. Since the results basically agree for 1,1,1-trichloroethane, chloroform and methylene chloride, full equilibrium was apparently reached in the stripping tower for these compounds at all temperatures. For tetrachloroethylene and trichloroethylene, the results indicate that equilibrium was barely complete at 10°C. As the temperature increased, so did the Henry's constants of these compounds, and this lowered the fraction of equilibrium achieved, causing an increasingly significant error in measured Henry's constants. Equation (17) shows that increases in Henry's constant would tend to decrease the fraction of equilibrium achieved in bubble columns. Assuming that the exponential model of approach to equilibrium (Equation 17) is correct, the stripping tower would have had to have been twice as tall (approximately 1 meter) in order to measure Henry's constants within 5 percent for tetrachloroethylene and trichloroethylene at 30°C. It would have had to have

been 1.5 meters tall in order to achieve more than 99 percent of equilibrium and measure Henry's constants for these compounds within 1 percent. In such a tall tower, it might be difficult to ensure complete mixing.

EPICS is a superior method for determining the Henry's constants of volatile compounds because it is not constrained by the limits of the batch air-stripping apparatus. The stripping tower used in these experiments, which was among the tallest reported in the literature, was adequate for determining the Henry's constants of four compounds (1,1,1-trichloroethane, chloroform, methylene chloride, and presumably, o-dichlorobenzene) but inadequate for tetrachloroethylene and trichloroethylene. In batch air stripping, the time available for the gas bubbles to reach equilibrium is fixed by the height of the tower. With EPICS, there is no limit on the time available for reaching equilibrium because closed systems are used.

2. Mixed Organic and Phenol Experiments

The results of the mixed organic and phenol experiments are very interesting and suggest a number of conclusions.

- The EPICS results demonstrate that the Henry's constants of the common volatile pollutants are not affected by the presence of other organics at the concentrations used in these studies.
- The common research practice of measuring Henry's constants by batch air stripping in mixtures may lead to erroneously high values.
- Henry's constant measurements in batch air-stripping towers are probably, as Munz and Roberts (1982) reported, affected by changes in mass transfer coefficients, and this implies that there is a deficiency in the derivation of the batch air-stripping technique.

The batch air-stripping results show significant (> 10 percent) increases in measured Henry's constants compared to the batch air-stripping values obtained in distilled water for two compounds in

the low-concentration mixture, four compounds in the high-concentration mixture, and all six compounds in 200 mg/l phenol. The EPICS results prove that the batch air-stripping mixture and phenol results are incorrect. The EPICS results are convincing because the technique is simple. In the EPICS phenol studies, for example, two similar closed systems were compared. One contained distilled water, and the other contained 200 mg/l phenol, but both had identical liquid and gas volumes, and contained tne same mass of volatile organic. Since the equilibrium gas concentrations in the two systems were equal for all volatile compounds studied, there cannot have been any changes in Henry's constant, and the batch air-stripping results cannot be correct.

Some of the discrepancies between the results obtained by the two techniques for two of the compounds, tetrachloroethylene and trichloroethylene, are undoubtedly due to the fact that at 25°C, the batch air-stripping tower did not reach equilibrium for these compounds. As mentioned in the experimental procedures section, the solution of 200 mg/l phenol and the six-component mixtures caused the air bubble size in the column to decrease, although there was no change in flow rate. A decrease in bubble diameter from 3 mm to 1 mm would cause an order-of-magnitude increase in the ratio of total surface area to gas flow rate (A^*/G). This would almost certainly bring the column to full equilibrium, and increase the Henry's constant measurements for tetrachloroethylene and trichloroethylene.

It is much harder to explain the batch air-stripping Henry's constant measurements in the mixture and phenol studies that are higher than the values obtained by EPICS in distilled water. For example, in the batch air-stripping experiments, both 200 mg/l phenol and the "high" concentration mixture increased the Henry's constant measurement for 1,1,1-trichloroethane by about 20 percent. However, the results of the Henry's constant measurements in distilled water by batch air stripping and EPICS agree for this compound, so the stripping column was apparently reaching full equilibrium. The changes in bubble size, caused by the presence of phenol, should therefore have had no effect.

The phenol solution and organic mixtures almost certainly caused changes in the mass transfer coefficients in the bubble column, since the changes in bubble size indicate changes in surface tension. But these changes should not have affected the Henry's constant measurements in the bubble column either. The overall, liquid-phase mass transfer coefficients (K_ℓ) and surface area parameters (A^*) appear in Equation (17) only. Once equilibrium is reached, Henry's constant is given by Equation (16) [or Equation (86)] alone.

Thus, the increases in Henry's constants measured by batch air stripping cannot be explained using the model given in Equations (16) and (17). Munz and Roberts (1982) reported that Henry's constant determinations -- in air-stripping columns operated at equilibrium -- are still affected by changes in mass transfer coefficients. The results of these phenol and organic mixture studies support that finding. Since an equilibrium constant cannot be affected by kinetic parameters, and the EPICS results prove that Henry's constants were not affected, it seems likely that either there is a deficiency in the derivation of the batch air-stripping technique, or one of the seven theoretical assumptions upon which it is based, is invalid.

In conclusion, these experiments suggest that mixtures should not be used when measuring Henry's constants in a batch air-stripping tower. Unfortunately, most reported Henry's constants for the common groundwater pollutants were determined in this manner.

3. Ionic Strength Studies

The results of the ionic strength studies indicate that,while increasing ionic strength does increase effective Henry's constants for volatile pollutants, the effects will have no significance for most groundwater applications. The EPICS results show that significant (> 10 percent) increases in effective Henry's constant do not occur until the ionic strength is greater than 0.26. While higher salt concentrations might be found in industrial or coastal situations, they are not likely to be found in groundwater.

The results of the EPICS and batch air-stripping experiments agree fairly well, except for tetrachloroethylene. The differences in

results obtained for tetrachloroethylene, shown in Figure 10, are almost certainly due to the batch air stripping tower not achieving full equilibrium for this compound at 25°C and zero ionic strength (distilled water). As the ionic strength increased, Henry's constant increased slightly, as shown by the EPICS results, but the big increases in batch air-stripping measurements were undoubtedly caused by changes in bubble size. Increasing ionic strength caused a significant decrease in bubble size in the stripping tower. As discussed in the previous section, a decrease in bubble size with no change in gas flow rate would drive the column towards equilibrium and increase the measured Henry's constants. Once full equilibrium was reached, at about 0.2 M (KCl), the Henry's constant measurements basically agreed with the EPICS results.

4. Comparison of Henry's Constant Measurements with Reported Values

Reported values of Henry's constants vary widely, particularly those estimated from vapor pressure and solubility data. Kavanaugh and Trussell (1980), Leighton and Calo (1981), and Munz and Roberts (1982) have published measured Henry's constant data for some of the compounds studied here.

Kavanaugh and Trussell list Henry's constant temperature regression equations for tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, and chloroform. Leighton and Calo give regression equations for 21 compounds including all those studied here except o-dichlorobenzene. A comparison of these regressions with those listed in Tables 10 and 11 show that all results for one compound, chloroform, agree within 10 percent. For the other compounds, Leighton and Calo's regressions agree quite closely with those obtained here, while Kavanaugh and Trussell's do not. A sample comparison of temperature regressions is shown in Figure 14.

Kavanaugh and Trussell do not provide an experimental procedure, so it is not possible to explain the discrepancies between their regressions and those obtained here and by Leighton and Calo. Leighton and Calo used a complex procedure, which involved both

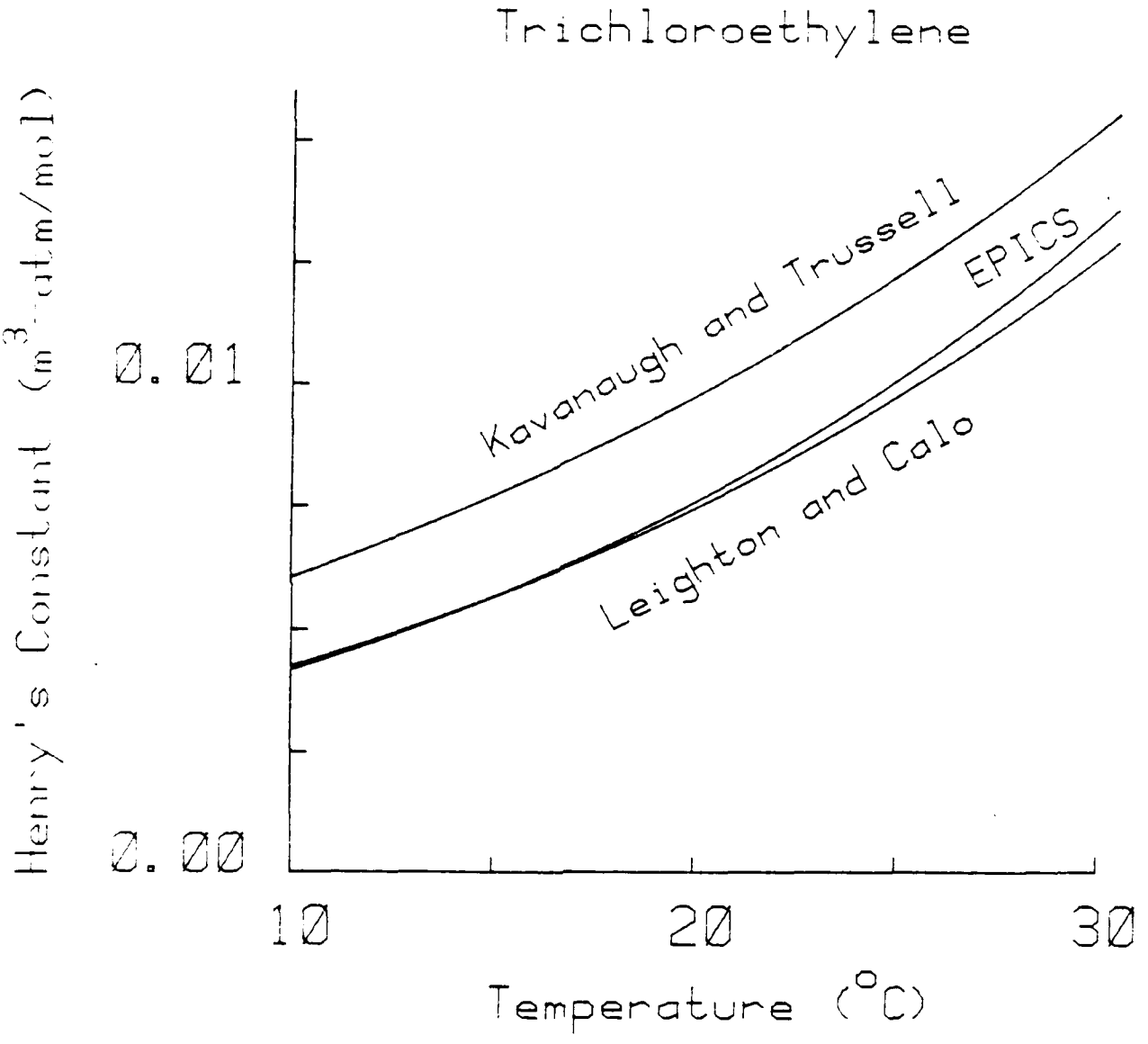

Figure 14. Comparison of the EPICS Temperature Regression for Trichloroethylene with Literature Reports.

stripping and the measurement of concentrations in both phases, and there is substantial agreement between their results and those obtained by the simpler EPICS procedure. The most significant differences between Leighton and Calo's results and the EPICS results are for methylene chloride at 10°C, where Leighton and Calo's value for Henry's constant is 24 percent higher than the EPICS value. The difference is probably due to an error in Leighton and Calo's technique. Leighton and Calo measured Henry's constants for methylene chloride in a mixture that also contained six other compounds at unspecified concentrations. The mixed organic and phenol experiments, performed here, show that the use of mixtures in stripping experiments can cause unpredictable increases in Henry's constant measurements.

Munz and Roberts measured Henry's constants for tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, and chloroform at 20°C, using both a batch stripping tower and a closed-system technique which required concentration measurements in both phases. The batch air-stripping values are significantly higher than the EPICS results (up to 70 percent), but since they were measured in a mixture of eight compounds, they are probably erroneous. Munz and Roberts discount their closed-system values, which have poor precision, as unreliable; however, they all are within 15 percent of the EPICS values.

SECTION V

DIFFUSIVITY MEASUREMENTS

A. OBJECTIVES AND PROGRAM OF STUDY

One important parameter affecting $K_\ell a$ is the liquid-phase diffusivity (D_ℓ) of the compound being stripped. The various $K_\ell a$ correlations require D_ℓ values as input. However, as outlined earlier, reliable, experimentally measured diffusivities are unavailable for compounds of interest to these studies. Thus, empirical diffusivity correlations must generally be employed. Several of these correlations are in common use, yielding a range of D_ℓ values for any given compound and temperature.

The objective of this phase of study was to provide experimental measurements of D_ℓ for the five primary compounds of interest, to evaluate the various diffusivity correlations available. A diaphragm cell method was employed, with all experiments being performed at 20°C, using dilute mixtures of the five study compounds.

B. PROCEDURES

1. Diffusion Cells

Diffusion measurements were obtained using a modified version of the horizontal diaphragm cell described by Holmes (1960). Although vertically oriented chambers have been used more frequently in the past, horizontal cells have been used successfully when density differences between the two cell chambers are small (Holmes, 1960; Byers and King, 1966; Chandrasekaran and King, 1972). Operation with the cells horizontal allows ease of filling and sampling, and the cell constant (B) is not sensitive to small amounts of air on the diaphragm.

Each of the three diffusion cells, consisting of two solution chambers separated by a vertical fritted glass diaphragm, was constructed from a 5 cm diameter glass sealing tube (Ace Glass, Inc.) with a diaphragm of porosity D (10-20 μm). When density differences between the two sides are small, this pore diameter prevents mass

transfer from free convection through the diaphragm, while being sufficiently large in comparison with molecular dimensions to permit diffusion to proceeed under conditions comparable to free diffusion (Gordon, 1945). As shown in Figure 15, sampling ports located in the top center of each chamber allowed headspace sampling of concentrations in the two chambers. The cells were sealed with Teflon®-lined silicone septa and plastic screw caps with holes punched through them to allow sampling by syringe. The cell volumes, as reported in Table 18, were determined gravimetrically. When weighed, each cell contained a 2.4 cm by 0.95 cm Teflon®-coated, egg-shaped stir bar in each chamber to simulate experimental conditions.

Background on the diaphragm cell method has been presented in Section II. N.

2. Stirring and Temperature Control

For each diffusion experiment, two cells were placed inside a 50-liter steel-belted Coleman cooler in a 20°C constant-temperature room. The experimental apparatus (Figure 16) was constructed inside the cooler for possible future work at different temperatures, using a refrigeration unit attached to the cooler. Two wooden dowels supported each cell 0.635 cm (1/4 inch) above the magnetic stirrers. Rubber bands held each cell in place, inhibiting rotation or longitudinal movement along the dowels. Two magnetic stirrers were assembled in series for mixing each cell by mounting magnets on enclosed spiral bevel gears (Hub City Model AD1, 1:1 ratio). The center of each magnet corresponded approximately to the center line of a diffusion cell chamber. A Masterflex® variable-speed drive mounted on the outside of the cooler approximately 13 cm (5 inches) above its base rotated the magnetic stirrers. The variable-speed drive was capable of operation at from 6-600 rpm.

3. Compounds

Diffusivities were determined for the same five compounds used in the later air-stripping experiments: 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene, chloroform, and methylene

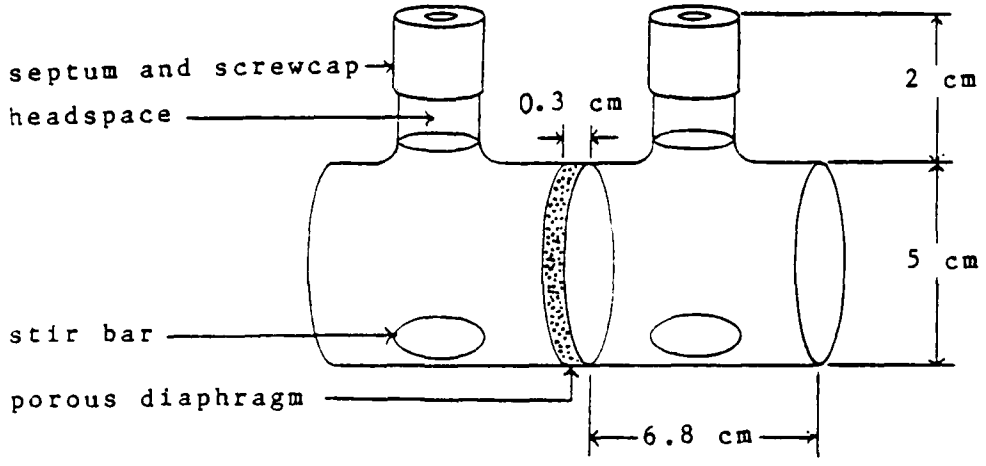

Figure 15. Diaphragm Diffusion Cell.

TABLE 18. VOLUME OF THE DIFFUSION CELLS

	Volume of Side A (cm^3)	Volume of Side B (cm^3)	Total Cell Volume (cm^3)
Cell 1			
liquid volume	136.5	144.4	
gas headspace	4.9	5.1	
Total	141.4	149.5	290.9
Cell 2			
liquid volume	142.2	135.9	
gas headspace	6.3	5.8	
Total	148.5	141.7	290.2
Cell 3			
liquid volume	140.0	137.7	
gas headspace	4.4	5.3	
Total	144.4	143.0	287.4

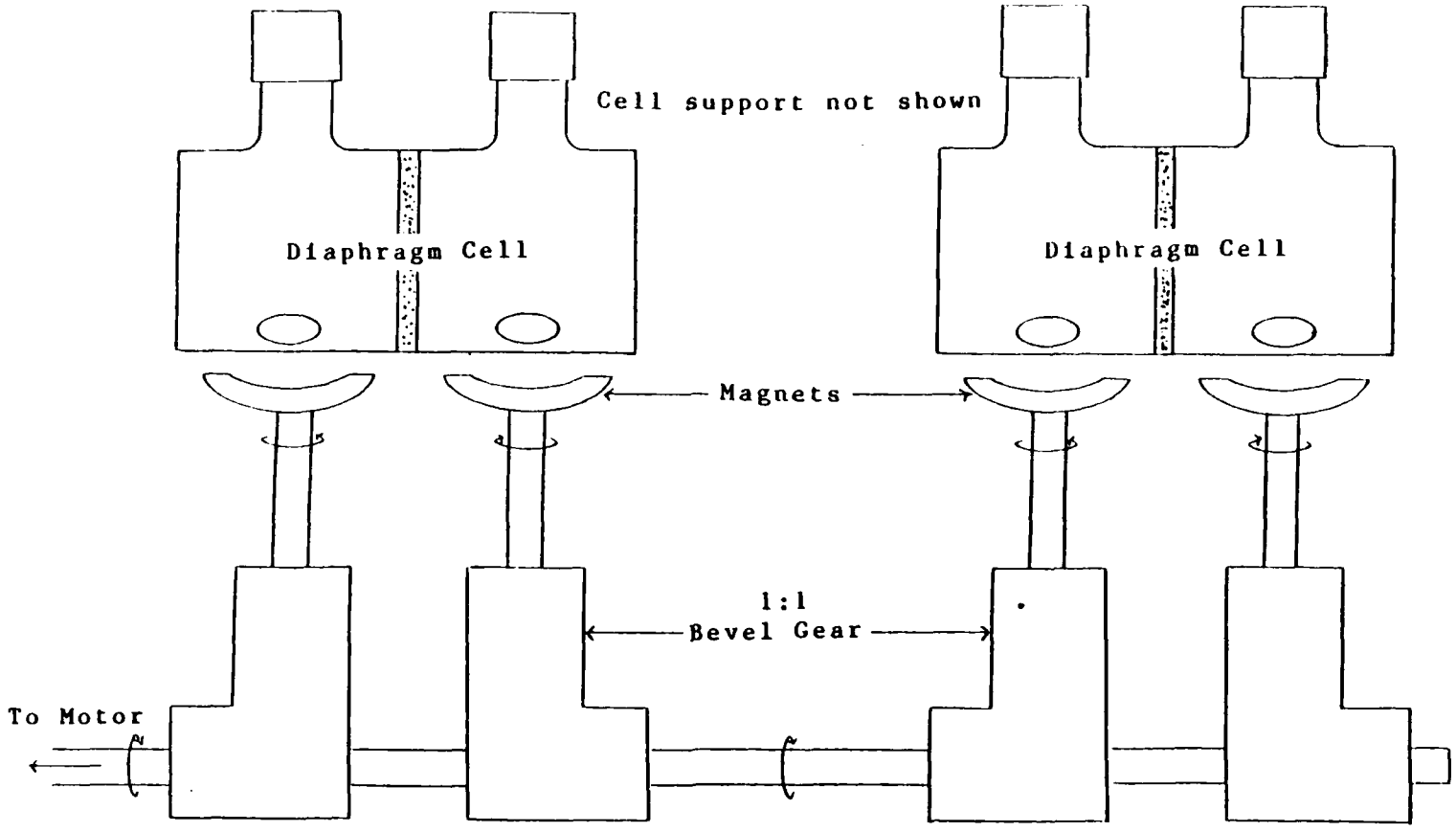

Figure 16. Schematic of Diaphragm Cell Apparatus.

chloride. An organic stock solution was prepared fresh for each experiment using degassed, deionized-distilled water. Deionized-distilled water was used primarily to prevent clogging of the diaphragm. Degassing (to avoid bubble formation in the diffusion cell) was accomplished by boiling the water in 3-liter boiling flasks, then transferring the hot water to a 5-liter side-arm flask. The flask was sealed with a rubber stopper and allowed to cool approximately 1 hour. The organics were added to the still warm water (to aid dissolution); degassed, deionized-distilled water was added to completely fill the flask; a Parafilm-covered rubber stopper was inserted; and the solution was stirred on a magnetic stirrer until the organics had dissolved. The solution was transferred to a constant-temperature room and allowed to cool to 20°C. The approximate concentrations of the organics in the stock solution are listed in Table 19.

Hydrochloric acid was used to calibrate the cell. A 0.203N stock solution was prepared by adding 80 ml of approximately 12N HCl to roughly 4.6 liters of degassed, deionized-distilled water. A 0.25 NaOH titrant was used after being standardized with 1N HCl (guaranteed normality = 0.999 - 1.002N).

4. Sample Analysis

The gas chromatograph used and the conditions of use in sample analysis were the same as described in Section III.

5. Experimental Procedures

The diffusion study was carried out in roughly three phases: preliminary experiments to clarify experimental procedures, calibration of the diffusion cells, and actual determination of the diffusivities of each of the five organics using two sampling procedures. All of the experiments were performed at 20°C. Solutions in each cell chamber were stirred at 300 rpm.

Preliminary experiments were performed using the same basic procedures that were later followed in the main experiments. Experimental conditions were not controlled as stringently in these initial runs -- the main departures being that the stock solutions

TABLE 19. ORGANIC SOLUTION FOR DIFFUSIVITY EXPERIMENTS

	Vol. Added to 5 l Water (µl)	Approximate Concentration (mg/l)	Approximate Mole Fraction ($\times 10^{-7}$)
methylene chloride	15-25	3.5 - 7.2	7.3 - 15.0
chloroform	15-20	4.9 - 6.5	7.3 - 9.8
tetrachloroethylene	15-25	5.3 - 8.9	5.8 - 9.6
trichloroethylene	15-17	4.8 - 5.4	6.6 - 7.5
1,1,1-trichloroethane	6-7	1.7 - 2.0	2.4 - 2.7

were not outgassed in the first of these experiments, and minor temperature adjustments were made during the course of both experiments. The first preliminary experiment was initiated in the constant-temperature, 20°C room with a 7.6 cm (3-inch) thermal buffer of water in the bottom of the ice chest and the cooler lid closed. However, mechanical heat generated by the gears and evaporative cooling of the water made more precise temperature control possible with the cooler operated dry and open in the constant temperature room. All subsequent runs were performed under these conditions.

As noted in Section II, reliable results are obtained more readily when the final difference in concentration between the two cell chambers is approximately half the initial difference. As determined in the two preliminary experiments, a 3-day period allowed this condition to be achieved for most of the compounds under study, while maintaining a measurable concentration difference between the two chambers for all compounds. The actual results presented in Table 20 show that 1,1,1-trichloroethane and chloroform had approximately reached the desired ratio after roughly 3 days, while methylene chloride fell short of a ratio of 2, and trichloroethylene and tetrachloroethylene were significantly past the desired end point, with concentration ratios of 3 and 7, respectively. Hence, a 3-day experimental run seemed the best compromise.

The optimum stock solution was determined by varying the concentrations used in these early experiments. The sampling frequency of twice per day used in the first two diffusion experiments was also determined from these preliminary results. Volume changes were observed when sampling during the first preliminary experiment. Subsequently, both chambers were vented when sampling during the rest of the experiments to equalize pressures in the two chambers.

Before beginning a diffusion or calibration experiment, the temperatures of the diffusion cells and all liquids used were brought to 20.0°C. The stirrers were started at 300 rpm at least 12 hours prior to the beginning of the experiment to allow for temperature adjustments due to mechanical heat generated by the gears. After this

TABLE 20. RESULTS OF PRELIMINARY EXPERIMENTS

Compound	Avg. $\frac{\Delta C_o}{\Delta C_t}$ (after three days)
Methylene Chloride	1.6
Chloroform	1.8
1,1,1-trichloroethane	1.9
Trichloroethylene	3.0
Tetrachloroethylene	7.0

equilibration period, the diaphragm of each cell was flushed repeatedly with degassed, deionized-distilled water to remove all air from the pores and establish the correct initial conditions (i.e., no solute in the diaphragm). One side of the cell was then drained and capped. Water was added to the other chamber (the "lean" side) and the chamber was sealed with a Teflon®-lined silicone septum and screw cap. The organic solution was added to the same level in the empty side (the "heavy" side), and it was quickly sealed with a septum and screw cap. The time was recorded as the cell was placed on the stirring apparatus.

The two cells used in the organic diffusivity experiments were calibrated three times, each calibration run lasting 3 days, The cells were prepared and thermal equilibrium was established as previously described. The initial concentration was established by titrating a 25 ml sample of the stock HCl solution with 0.25N NaOH to a phenolphthalein end point. Since one chamber was pure solvent (water), the concentration of the stock solution should equal ΔC_0. After diffusion had proceeded for 3 days, 20 ml samples were withdrawn simultaneously from each side of the diffusion cell and concentrations determined using the same titration procedure. Three replicates of both the initial and final concentrations were used in calculations for each experiment. The cell constant, B, was calculated using the modified diaphragm cell equation, Equation (82), with $H_c = 0$.

Diffusivities were obtained from Stokes (1950b) for hydrochloric acid at 25°C and adjusted to 20°C assuming $D_\ell \mu_\ell / T$ is constant. At the acid concentration used, the diffusivity obtained is an integral diffusion coefficient, not a differential diffusion coefficient (see Section II. L); therefore, the diffusivity value depends on the initial concentration. Stokes obtained integral diffusivities at 25°C of 3.058×10^{-5} $cm^2 \cdot s^{-1}$ and 3.055×10^{-5} $cm^2 \cdot s^{-1}$ for initial concentration differences of 0.2020N and 0.3030N HCl, respectively. Therefore, the integral diffusivity for a 0.203N HCl solution at 25°C is 3.058×10^{-5} $cm^2 \cdot s^{-1}$. This value must be adjusted for temperature. If:

$$D_{\ell}^{298} \mu_{\ell}^{298}/298°K = D_{\ell}^{293} \mu_{\ell}^{293}/293°K$$

Then:

$$D_{\ell}^{293} = \frac{293\ (3.058 \times 10^{-5})\ (0.890)}{298\ (1.002)} = 2.671 \times 10^{-5}\ cm^2 \cdot s^{-1}$$

The results of the cell calibrations are presented in Table 21. The cell constant is not dimensionless. The constants presented in Table 21, when used in Equation (82), will yield diffusivities in $cm^2 \cdot s^{-1}$ when time is evaluated in seconds and cell volumes are in cubic centimeters.

In the first two organic diffusion experiments, samples were taken in a repeating pattern of 10-hour and 14-hour intervals, resulting in seven samples over the 3 days of the experiment. Sampling began roughly 10 hours after the cells had been flushed, filled, and placed on the stirring apparatus. The initial 10-hour delay prior to sampling ensured that a linear concentration gradient in the diffusion cells had been established. Since the organic concentration in the cells could not be determined at the time the cells were placed on the stirrers due to the equilibrium constraints of gas-phase and liquid-phase partitioning, the concentration difference determined after 10 hours of diffusion was the initial concentration difference (ΔC_0). Timing of the diffusion experiment began with this sample.

For each sampling period, relative liquid concentrations on either side of the diaphragm were determined from headspace samples. Immediately prior to sampling, two side-port needles simultaneously pierced the septa on both sampling ports to relieve any pressure changes since the last sampling period and pressure changes during sampling that might induce bulk flow through the diaphragm. With the venting needles still inserted, a 0.5 ml sample was withdrawn from the lean side of that cell and injected into the gas chromatograph. The procedure was repeated for the lean side of the second cell before the heavy side of the first cell was sampled. The venting needles were withdrawn immediately after a sample was taken and reinserted in the same manner before the heavy side was sampled. At the end of 72 hours, the results were analyzed using Equation (82) presented in

TABLE 21. DIFFUSION CELL CONSTANTS (B)

	Expt. 1	Expt. 2	Expt. 3	Avg. B
Cell 1	5.95	6.02	5.91	5.96
Cell 2	6.12	6.37	5.94	6.13

Section II. The cells were thoroughly rinsed with deionized-distilled water and thermally equilibrated before another experiment began.

Mass losses in these first two experiments prompted procedural modifications in the remaining experiments. In two experiments, concentrations were determined only once after 72 hours. The initial concentration difference was obtained by back-calculation, using the mass determined from these samples. These calculations are explained in more detail in the "Results" portion of this section.

In the last diffusion experiment, no initial concentrations were obtained directly from the two cells placed on the magnetic stirrers as in the two experiments described above. Initial concentration differences and the total masses in the systems were obtained from the third cell (c ck-up) not normally used in these experiments. Both chambers of this cell were filled with the organic stock solution, the cell was hand shaken, and allowed to equilibrate to 20 minutes. Samples were then taken from each side of the cell and used to determine the initial mass and concentration differences for the other two cells. (The validity of the procedure was evaluated by filling all three cells with the same stock solution and comparing peak heights from the gas chromatograph). A detailed discussion of the mass correction is presented later in Section V. C.

The third cell was also sampled at the end of the 72-hour run, providing mass-loss data for comparison with mass losses in the first two experiments.

C. RESULTS

1. The First Two Diffusivity Experiments

The results of the first two experiments, when the cells were sampled twice each day, are presented in Table 22. Diffusivities were calculated from the measured concentration differences using Equation (82). The values are remarkably higher than the diffusivity estimates obtained using empirical correlations (Table 3), especially when comparing diffusivities for 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene. There is also a significant amount of variation in the measured diffusivities for each compound. Volume

TABLE 22. MEASURED DIFFUSIVITIES -- FIRST TWO EXPERIMENTS

Compound	Cell 1 - Exp 1 D	r^2	n[a]	Cell 1 - Exp 2 D	r^2	n	Cell 2 - Exp 1 D	r^2	n	Cell 2 - Exp 2 D	r^2	n
	(diffusivity units = 10^{-5} cm^2/s)											
methylene chloride	1.63	0.99	6	0.97	0.94	6	1.16	0.93	6	1.20	0.97	7
chloroform	1.99	0.99	6	1.14	0.94	7	1.53	0.96	6	1.39	0.97	7
1,1,1-trichloroethane	4.91	1.00	6	2.83	0.97	7	3.14	0.98	6	3.13	0.99	7
trichloroethylene	4.45	1.00	6	3.20	0.97	7	3.88	0.99	5	3.70	1.00	7
tetrachloroethylene	7.29	1.00	6	6.88	0.97	7	7.15	0.99	6	7.61	1.00	7

[a] n = number of samples

changes in the diffusion cells could account for some of the experimental variation, but not for the discrepancy between these values and those predicted by established correlations. Furthermore, the order of diffusivities contradicts the order obtained using the correlations. An examination of the mass in the system over the three-day experiment reveals the major source of the problem.

A measure of the mass of each compound in the diffusion cell can be calculated from:

$$M = p' \left[V'_g + \frac{V'_\ell}{H_c}\right] + p'' \left[V''_g + \frac{V''_\ell}{H_c}\right] \qquad (87)$$

where:

M = mass (relative units)

p', p" = GC peak heights for chambers 1 and 2, respectively.

The differences in initial and final masses, shown in Table 23, explain the high apparent diffusivities calculated from the gas chromatograph peak heights for 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene. Mass losses for these three compounds ranged from 34 to 79 percent, increasing roughly with compound volatility. Similar mass losses were reported by Dietz and Singley (1979) in their development of headspace gas chromatography for the analysis of volatile organics. Dietz and Singley reported losses of tetrachloroethylene, carbon tetrachloride, trichloroethylene, and chloroform from 125 ml vials once the septum had been pierced, noting that tetrachloroethylene exhibited the greatest losses. With three holes in the septum and letting the vial stand for 1.5 hours, tetrachloroethylene lost 11 percent of its mass.

2. Derivation of the Mass-Loss/Diffusion Equation

In order to determine if it was possible to correct for these losses, the mass remaining at each sampling time was plotted versus time on a semi-log scale. The approximate linearity of these plots (Figures 17 to 21) shows that the mass loss can be modelled as first-order with respect to the mass remaining, or:

$$\frac{dM}{dt} = -k_m M \qquad (88)$$

where:

TABLE 23. MASS LOSS IN DIFFUSION CELLS -- FIRST TWO EXPERIMENTS

		methylene-chloride	chloroform	1,1,1-tri-chloroethane	trichloro-ethlyene	tetrachloro-ethylene
Cell 1	Initial Mass[a]	1.96	2.60	1.31	2.92	5.49
Expt 1	Final Mass[b]	1.91	2.27	0.66	1.45	1.28
	% Loss	2.6	12.7	49.6	50.3	76.7
Cell 1	Initial Mass	4.77	3.75	2.29	3.96	1.45
Expt 2	Final Mass	5.00	3.67	1.49	2.33	0.37
	% Loss	- 4.8	2.1	34.9	41.2	74.5
Cell 2	Initial Mass	1.99	2.68	1.49	3.20	6.51
Expt 1	Final Mass	2.15	2.61	0.95	1.70	1.39
	% Loss	- 8.0	2.6	36.2	46.9	78.6
Cell 2	Initial Mass	4.74	3.71	2.23	3.85	1.42
Expt 2	Final Mass	5.02	3.70	1.47	2.45	0.33
	% Loss	- 5.7	0.3	34.1	36.4	76.8

[a] Mass reported in relative units.

[b] After three days at 20°C.

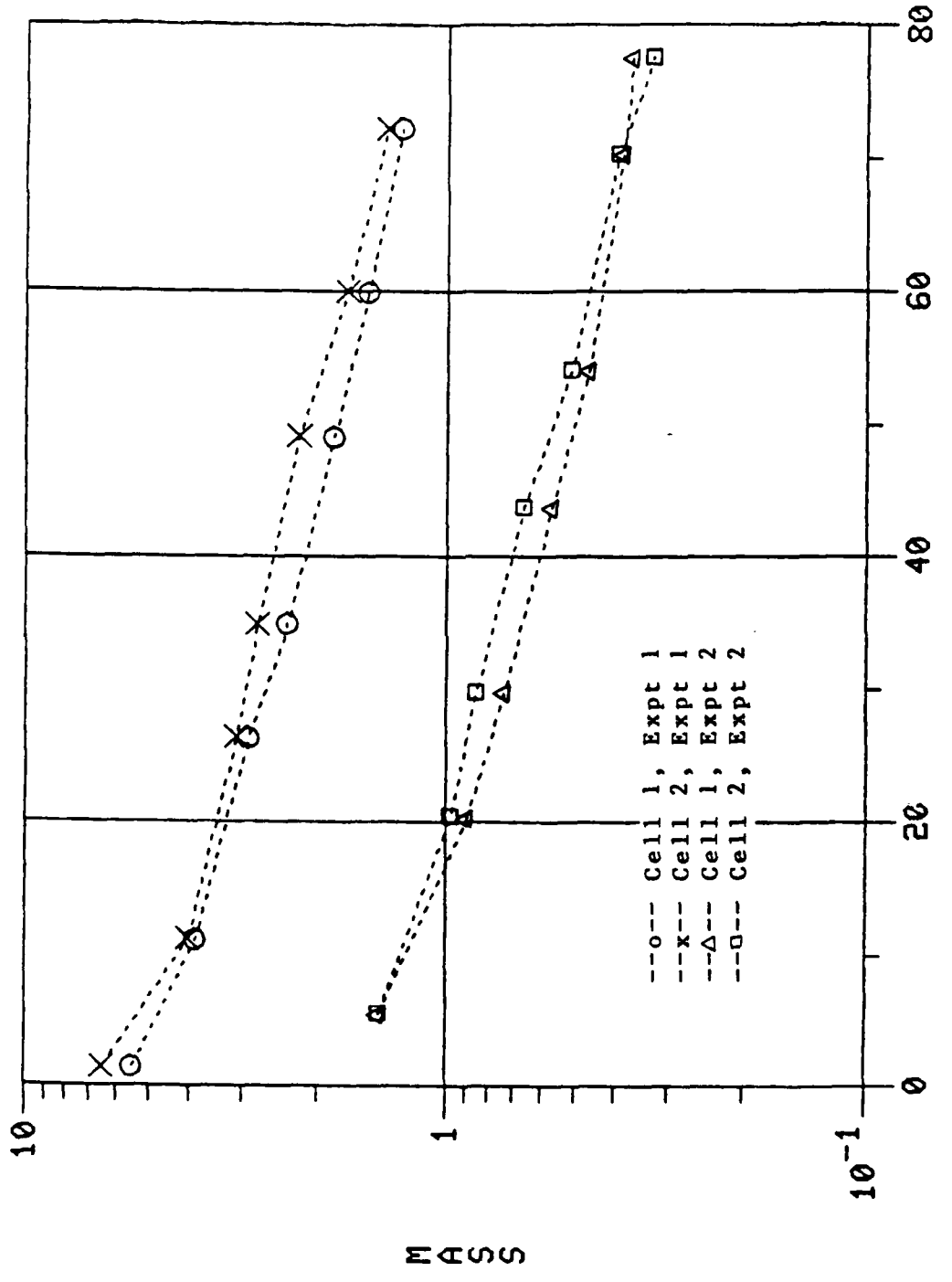

Figure 17. Diffusion Cell Mass Loss of Tetrachloroethylene.

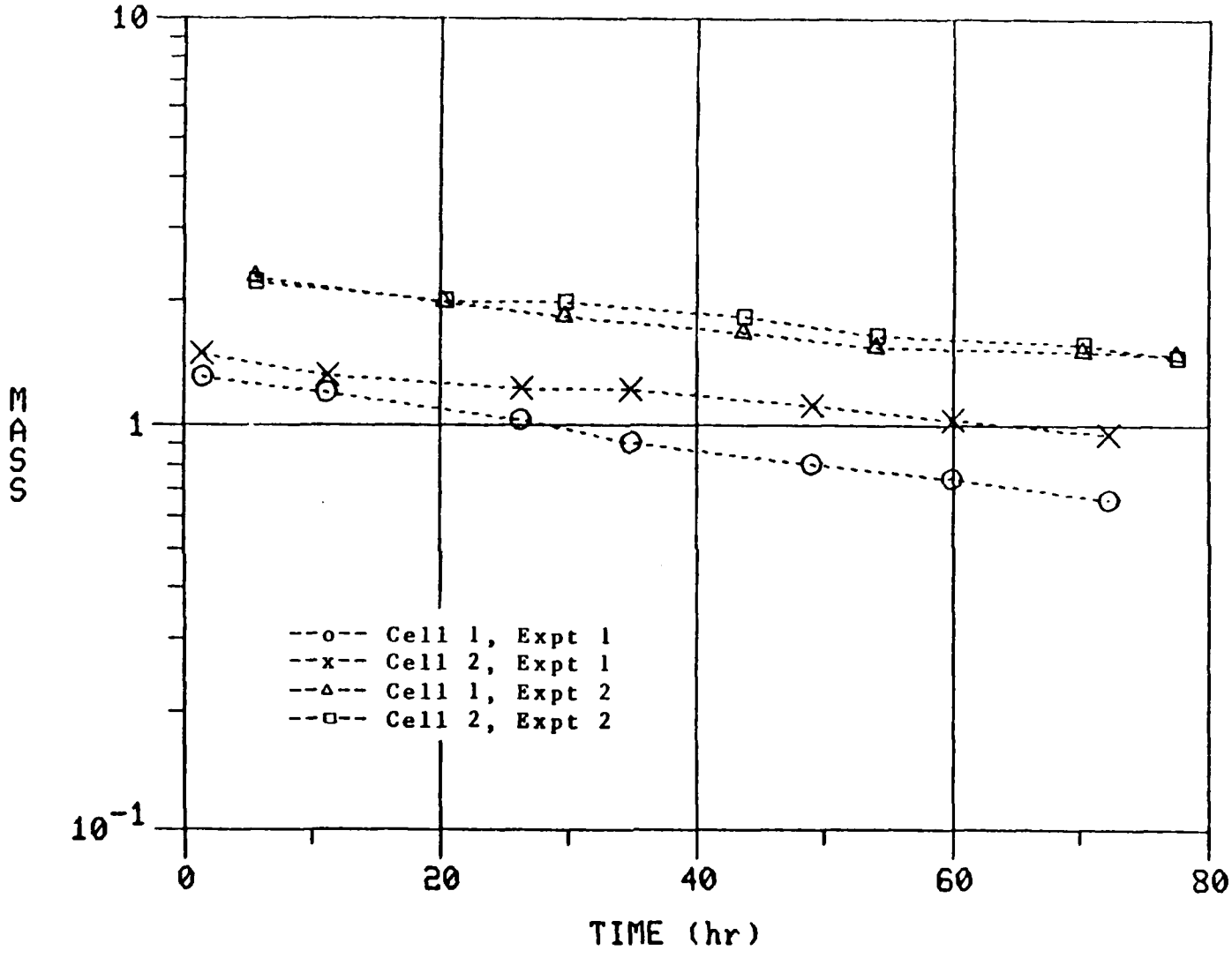

Figure 18. Diffusion Cell Mass Loss of 1,1,1-Trichloroethane.

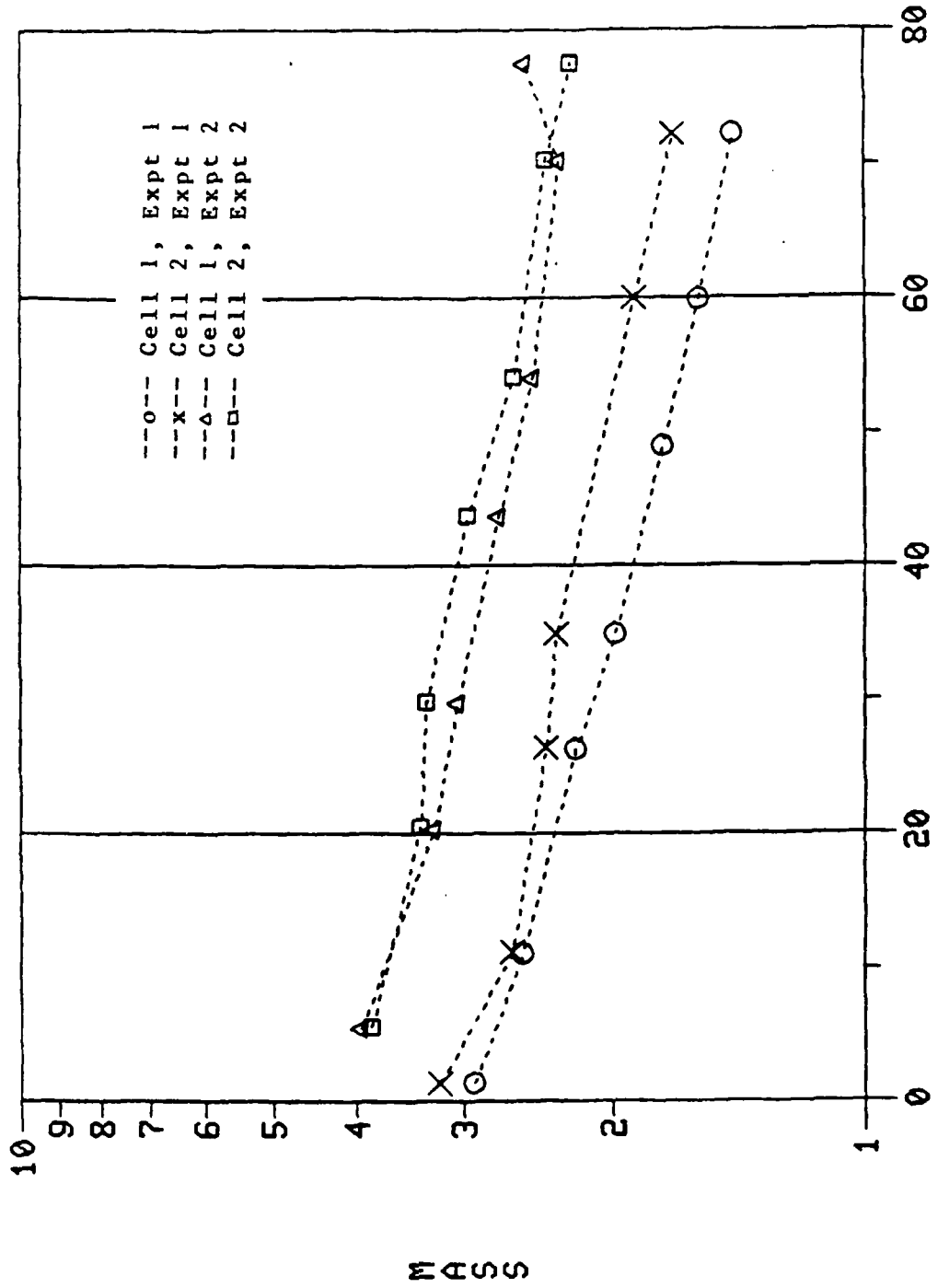

Figure 19. Diffusion Cell Mass Loss of Trichloroethylene.

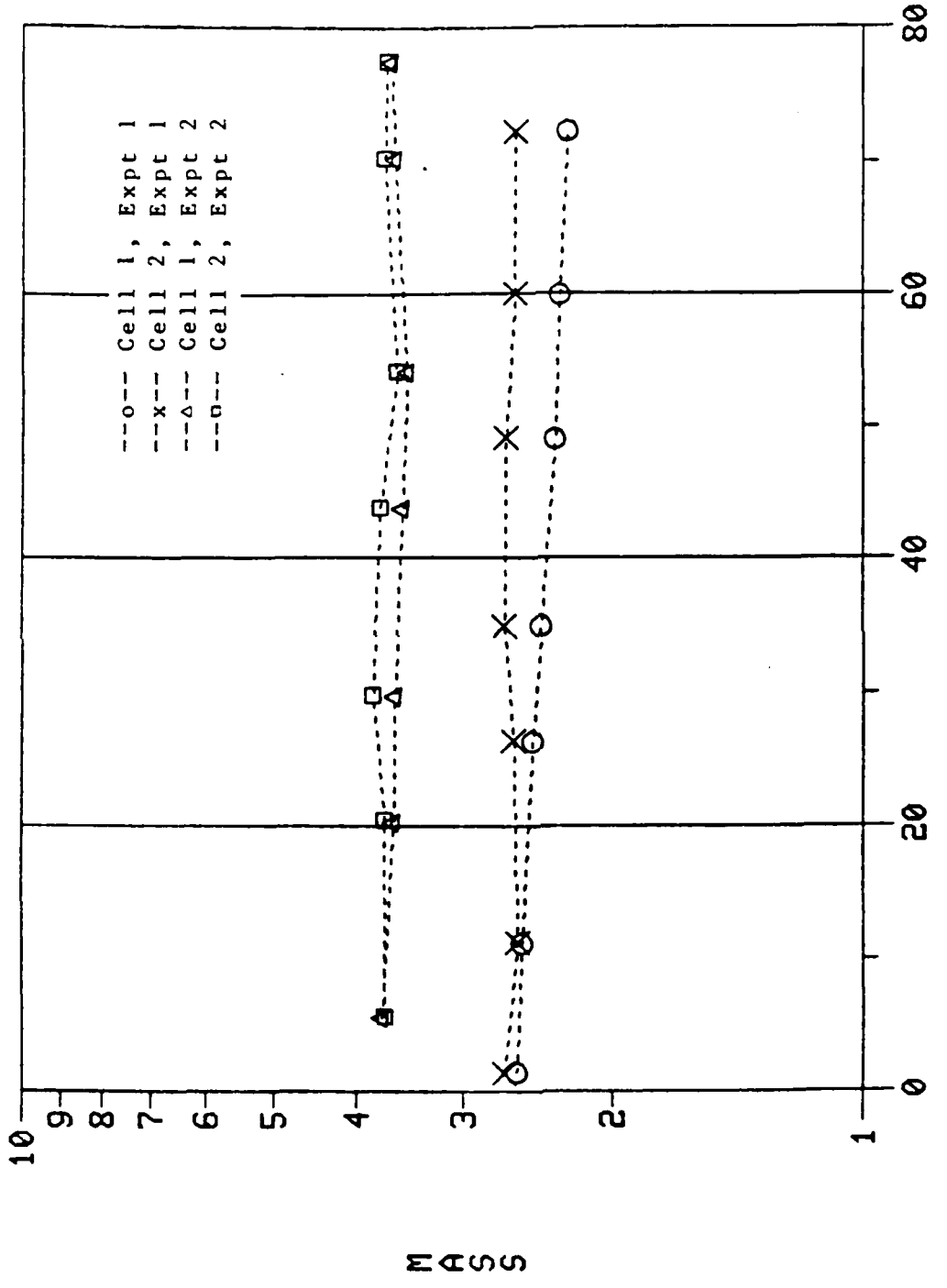

Figure 20. Diffusion Cell Mass Loss of Chloroform.

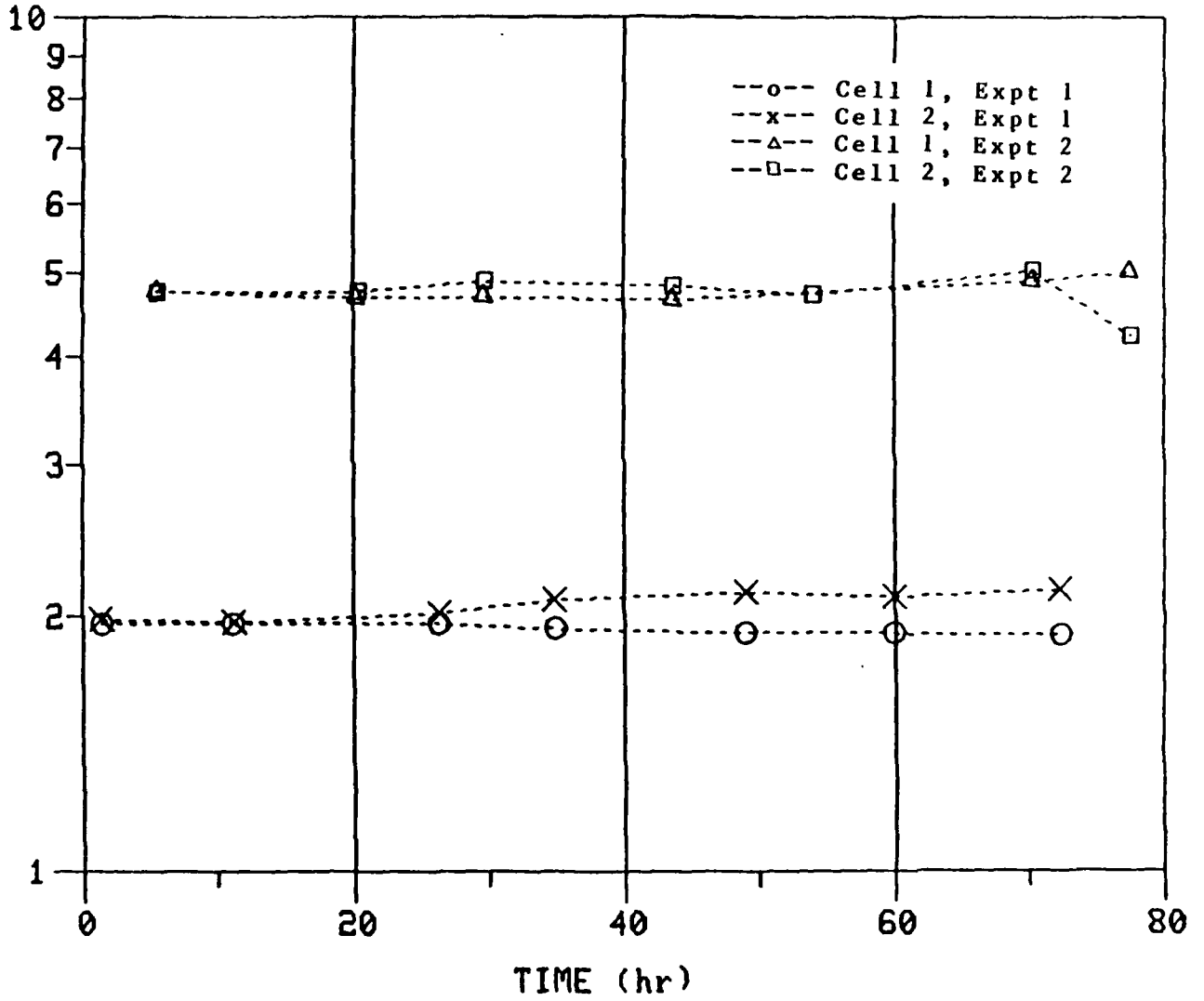

Figure 21. Diffusion Cell Mass Loss of Methylene Chloride.

k_m = mass loss constant (h^{-1}).

The diaphragm cell equation [Equation (82)] can be modified to account for the combined effects of mass loss and diffusion. Equation (82) was developed to account for gas- and liquid-phase partitioning of the solute. However, since $V_\ell \gg H_c V_g$, the actual mass in the headspace can be neglected, and the headspace peak height can be regarded as directly proportional to the aqueous concentration. This assumption is employed in the following derivation. As in all the derivations presented previously, rapid equilibrium between the two phases is assumed.

Molecular diffusion causes a change in concentration in each cell chamber that can be expressed for Side 1 as

$$\frac{dC'_\ell}{dt} = -\frac{DB}{V'_\ell}\,(C'_\ell - C''_\ell) \tag{89}$$

and for Side 2 as

$$\frac{dC''_\ell}{dt} = \frac{DB}{V''_\ell}\,(C'_\ell - C''_\ell) \tag{90}$$

The mass loss in the chamber is

$$\frac{dM}{dt} = \frac{dM'}{dt} + \frac{dM''}{dt} = -\left[V'_\ell k_m C'_\ell + V''_\ell k_m C''_\ell\right] \tag{91}$$

The combined effects of diffusion and mass loss are:

$$\text{Side 1:}\quad \frac{dC'_\ell}{dt} = \frac{-DB(C'_\ell - C''_\ell)}{V'_\ell} - k_m C'_\ell \tag{92}$$

$$\text{Side 2:}\quad \frac{dC''_\ell}{dt} = \frac{DB(C'_\ell - C''_\ell)}{V''_\ell} - k_m C''_\ell \tag{93}$$

The change in the concentration difference between the two chambers during time dt equals

$$\frac{d(C'_\ell - C''_\ell)}{dt} = \frac{dC'_\ell}{dt} - \frac{dC''_\ell}{dt}$$

$$= \frac{DB(C'_\ell - C''_\ell)}{V'_\ell} - k_m C'_\ell - \frac{DB(C'_\ell - C''_\ell)}{V''_\ell} + k_m C''_\ell$$

which simplifies to

$$\frac{d(C'_\ell - C''_\ell)}{dt} = (C'_\ell - C''_\ell)\left[-DB\left(\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right) - k_m\right]. \quad (94)$$

Dividing by $(C'_\ell - C''_\ell)/dt = \Delta C/dt$ and integrating yields

$$\int_{\Delta C_o}^{\Delta C_t} \frac{d\Delta C}{\Delta C} = -\int_o^t DB\left[\left(\frac{1}{V'_\ell} - \frac{1}{V''_\ell}\right) + k_m\right]dt$$

or

$$\ell n\left(\frac{\Delta C_t}{\Delta C_o}\right) = -\left[BD\left(\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right) + k_m\right]t. \quad (95)$$

This can be rearranged to

$$\Delta C_t = \Delta C_o \exp\left[-BD\left(\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right)t\right]\exp(-k_m t) \quad (96)$$

If F_t = the fraction of solute remaining at time $t = \exp(-k_m t)$, then

$$\Delta C_t = \Delta C_o \exp\left[-BDt\left(\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right)\right]F_t$$

or

$$\ell n\left(\frac{\Delta C_t/F_t}{\Delta C_o}\right) = -BDt\left[\frac{1}{V'_\ell} + \frac{1}{V''_\ell}\right]. \quad (97)$$

Including the headspace correction to the diaphragm cell equation gives

$$\ell n\left(\frac{\Delta C_t/F_t}{\Delta C_o}\right) = -BDt\left[\frac{1}{V'_\ell + H_c V'_g} + \frac{1}{V''_\ell + H_c V''_g}\right] \quad (98)$$

This form of the equation was used to calculate diffusivities corrected for mass loss. Instead of calculating the mass loss coefficient (k_m), the fraction of solute remaining was calculated from the change in mass in the diffusion cell by

$$F_t = \frac{p'_t\left[V'_g + \frac{V'_\ell}{H_c}\right] + p''_t\left[V''_g + \frac{V''_\ell}{H_c}\right]}{p'_o\left[V'_g + V'_\ell/H_c\right] + p''_o\left[V''_g + V''_\ell/H_c\right]} \quad (99)$$

A plot of

$$\ell n\left(\frac{\Delta C_t/F_t}{\Delta C_o}\right)$$

vs

$$- Bt\left[\frac{1}{V'_\ell + H_c V'_g} + \frac{1}{V''_\ell + H_c V''_g}\right]$$

should result in a line with slope = D.

3. Diffusivities Corrected for Mass Loss

Diffusivities corrected for mass loss are presented in Table 24. The results are compared to the uncorrected diffusivities in Table 25. The mass loss correction tended to increase the linearity of the regression and brought the magnitude of the diffusivities back in line with values calculated, using the correlations discussed earlier. With the exception of the results from Cell 1 in the first experiment, methylene chloride had the highest diffusivity, corresponding to the predictions of empirical correlations. No apparent order can be discerned for the other compounds, although the diffusivity for tetrachloroethylene does appear at the lower end of the scale. Diffusivities for all compounds except methylene chloride decreased when corrected for mass loss, as expected. The anomalous results for methylene chloride can be explained by referring to Table 23; methylene chloride gained apparent mass in three out of the four experiments. This increase in calculated mass is discussed in the next section.

In an attempt to eliminate the mass losses experienced when the cells were repeatedly sampled, concentrations were measured only once, after three days of diffusion, in the next three experiments. The total mass in the system was calculated according to Equation (87). Initially, all the solute was on one side of the diaphragm. Thus, the initial concentration difference (ΔC_o) could be determined from:

$$\Delta C_o = \frac{M_f}{V_{\ell o}/H_c + V_{go}} \qquad (100)$$

where:

V_{go}, $V_{\ell o}$ = gas and liquid volumes of the chamber initially containing solute;

M_f = mass calculated from the concentrations determined after 3 days of diffusion.

TABLE 24. DIFFUSIVITIES CORRECTED FOR MASS LOSS -- FIRST TWO EXPERIMENTS

Compound	Cell 1 - Expt 1 D	Cell 1 - Expt 1 r^2	Cell 1 - Expt 2 D	Cell 1 - Expt 2 r^2	Cell 2 - Expt 1 D	Cell 2 - Expt 1 r^2	Cell 2 - Expt 2 D	Cell 2 - Expt 2 r^2
	(diffusivity units = 10^{-5} cm^2/s)							
methylene chloride	1.47	0.994	1.24	0.998	1.60	0.984	1.44	0.999
chloroform	1.33	0.993	1.08	0.998	1.54	0.982	1.33	0.999
1,1,1-trichloroethane	1.68	0.995	0.960	0.996	1.44	0.982	1.31	0.999
trichloroethylene	1.36	0.996	0.933	0.997	1.58	0.979	1.33	0.998
tetrachloroethylene	1.24	0.992	0.953	0.995	1.58	0.976	1.22	0.994

TABLE 25. EFFECT OF MASS LOSS CORRECTION

Compound	Uncorrected $\bar{D}$ (10^{-5} cm^2/s)	Uncorrected CV%	Corrected for Mass Loss $\bar{D}$ (10^{-5} cm^2/s)	Corrected for Mass Loss CV%	Wilke-Chang Correlation X = 2.6 D (10^{-5} cm^2/s)
methylene chloride	1.24	22	1.44	10	1.21
chloroform	1.51	24	1.32	14	1.04
1,1,1-trichloroethane	3.50	27	1.35	22	0.905
trichloroethylene	3.81	14	1.30	21	0.945
tetrachloroethylene	7.23	4	1.25	21	0.855

The diffusivities measured from these last three experiments are shown in Table 26. On the average, methylene chloride had the highest measured diffusivity. As in the first two experiments, there is no discernible relative order among the other compounds. The magnitudesof the diffusivities for all compounds are notably higher than the values obtained when the cells were sampled repeatedly during one experiment. Coefficients of variation also tend to be larger than when the initial sampling procedure was used. This increased variability emphasizes the primary drawback to the second experimental method: the results depend on only one pair of samples.

4. Mass Loss Experiment

It was suspected that mass was lost even without piercing the septum, possibly due to solute sorption onto or through the septum's Teflon® lining. To determine if such losses did occur, the initial mass in each cell must be quantified without piercing the septum. If filled with the same solution, initial peak heights in all cells should be essentially equal, only differing slightly because of differences in headspace/liquid volume ratios among the cell chambers. The ratio of peak heights between any two cell chambers (F_g) with differing headspace and/or liquid volume is given by:

$$F_g = \frac{C_{gA}}{C_{gB}} = \frac{V_{\ell A}[H_c\ V_{gB} + V_{\ell B}]}{V_{\ell B}[H_c\ V_{gA} + V_{\ell A}]} \qquad (101)$$

where the subscripts A and B refer to the chambers being compared. Using either chamber of the third diffusion cell as the reference cell, the peak height ratios for the cells placed on the magnetic stirrers only vary between $0.991 \leq F_g \leq 1.003$, depending on which cell or compound is involved. Thus, within the limits of experimental precision, the initial concentration difference (ΔC_o) can be calculated from the peak heights obtained when the third cell is filled with stock solution.

This approach was verified experimentally by filling all chambers of the three cells with the stock solution, and then sampling the side that initially contained the stock solution in an actual experiment. The differences in peak heights between cells for each

TABLE 26. DIFFUSIVITIES -- LAST THREE EXPERIMENTS

	$D(10^{-5}\ cm^2/s)$ @ 20°C						
	Cell 2 Expt 3	Cell 1 Expt 4	Cell 2 Expt 4	Cell 1 Expt 5	Cell 2 Expt 5	$\bar{D}$	% CV
methylene chloride	1.93	1.21	1.58	1.56	2.05	1.67	20
chloroform	1.82	1.07	1.50	1.42	1.95	1.55	22
1,1,1-trichloroethane	1.84	0.968	1.48	1.47	2.13	1.58	28
trichloroethylene	1.53	1.02	1.53	1.70	1.92	1.54	22
tetrachloroethylene	1.88	0.989	1.50	1.82	1.90	1.62	24

compound (reported in Table 27) do not necessarily reflect limits in analytical accuracy. Rather, the measured peak heights reflect the order in which the cells were filled. As each cell was filled, the headspace in the 5-liter bottle containing the stock solution increased. Thus, volatilization losses cause peak heights to fluctuate between cells.

Using the peak heights from the third cell to estimate the initial mass, mass losses during the fifth diffusivity experiment are reported in Table 28. Even without puncturing the septum, mass losses from Cells 1 and 2 ranged from 14 to 30 percent, increasing roughly as compound volatility increased. The mass losses of each compound from the third cell (which was sampled both at the beginning and at the end of the experiment) ranged from 25 - 89 percent. These percentage losses from the third cell are larger than those calculated for the first two diffusion experiments (when samples were obtained twice per day). This higher percentage loss may at least be due partially to incorrect estimation of the initial masses in Cells 1 and 2 caused by changes in the headspace above the stock solution as the cells were filled.

Nevertheless, the main problem is not the difference in measured mass losses between experiments, but that mass was lost even without puncturing the septum. Blum (1984) determined that type TFE Teflon® sorbed tetrachloroethylene. Using the Teflon® coating on a rubber septum, Teflon® tape, and shavings from a Teflon®-coated magnetic stir bar, he reported 10 percent, 17 percent, and 59 percent tetrachloroethylene sorbed from the liquid phase, respectively, at 20°C with an equilibration period of 4 days. This supports the hypothesis that sorption onto or through the Teflon® lining causes at least some of the mass loss.

D. DISCUSSION

Since mass loss occurred even when the septum was only pierced for the final sample, no further attempts were made to measure diffusivities with this method. To compare the combined results of all five experiments with correlation estimates, the results using the two

TABLE 27. PEAK HEIGHT COMPARISON

	Peak Heights		
	Cell 1	Cell 2	Cell 3
methyiene chloride	34.3	36.7	37.8
chloroform	27.9	29.6	31.0
trichloroethylene	72.0	77.0	81.4
tetrachloroethylene	37.5	41.8	48.0
1,1,1-trichloroethane	56.4	62.0	70.9

TABLE 28. MASS LOSS EXPERIMENT RESULTS (72 hours)

Compound	Cell 1			Cell 2			Chamber 3A[a]			Chamber 3B[a]		
	Initial Mass[b]	Final Mass	% Loss	Initial Mass	Final Mass	% Loss	Initial Mass	Final Mass	% Loss	Initial Loss	Final Loss	% Loss
methylene chloride	3.63	3.11	14	3.62	3.08	15	248	181	27	248	185	25
chloroform	1.31	1.09	17	1.28	1.10	14	132	80	39	133	80	40
1,1,1-trichloroethane	1.61	1.28	20	1.61	1.37	15	638	211	67	631	203	68
trichloroethylene	0.745	0.583	22	0.743	0.613	18	170	50	71	173	46	73
tetrachloroethylene	0.735	0.521	29	0.734	0.566	23	286	35	88	285	32	89

[a] Chambers 3A and 3B - septum pierced to obtain initial concentration.

[b] Mass in relative units.

sampling procedures must be combined. Using a Mann-Whitney non-parametric test (Snedecor and Cochran, 1980), the null hypothesis that the two samples were from the same population could not be rejected at the 95 percent confidence level. The results from the two types of diffusivity experiments were averaged by weighting the values from the multiple-sample experiments five times greater than the other diffusivity values (based on the average number of points used in the regression to determine diffusivity in the first type of experiment). These results are compared to the correlation estimates in Table 29. The average of the diffusivities obtained experimentally for all compounds is higher than the correlation estimates. Methylene chloride appears to have the highest diffusivity, but there is no clear difference between the average diffusivities for the other compounds. This contrasts with the correlation estimates, which predict that the diffusivity for chloroform is approximately 22 percent greater than the diffusivity for tetrachloroethylene. Methylene chloride's diffusivity is estimated to be 40 percent greater than tetrachloroethylene's, not 12 percent greater as determined experimentally. Thus, the results indicate less variability in diffusivities than predicted by the correlations. However, these experimental results are too uncertain to allow definite conclusions. There is more variation among diffusivity values for one compound in the five experiments (typical CV $\approx$ 20 percent) than among diffusivities from one cell for all five compounds during a single experiment (typical CV $<$ 10 percent), no matter which sampling procedure was followed.

In summary, we were unable to measure diffusivities with precision exceeding the reported accuracies of the correlations. Until more accurate measurements of diffusivities are obtained for these compounds, using a method that eliminates the mass losses observed in this study, empirical correlations should probably be used to estimate diffusivities. Nothing in these experimental results contraindicates their use.

TABLE 29. MEASURED AND CALCULATED AQUEOUS-PHASE DIFFUSIVITIES

Compound	D (10^{-5} cm^2/s at 20°C)[a] Measured Mean	Wilke-Chang X = 2.6	Othmer and Thakar	Scheibel	Hayduk and Laudie	Wilke-Chang X = 2.26
methylene chloride	1.48	1.21	1.12	1.14	1.13	1.12
chloroform	1.37	1.04	0.98	0.97	0.98	0.97
trichloroethylene	1.35	0.95	0.89	0.88	0.89	0.88
1,1,1-trichloroethane	1.39	0.91	0.85	0.84	0.85	0.83
tetrachloroethylene	1.32	0.86	0.81	0.80	0.80	0.80

[a] LeBas molar volumes used

SECTION VI

PACKED-TOWER AIR-STRIPPING STUDIES

A. OBJECTIVES AND PROGRAM OF STUDY

The purpose of this study was to evaluate the accuracy of the Onda correlations for predicting overall mass transfer coefficients in packed-tower air stripping of dilute, volatile organics over a range of operating conditions and packing types representative of expected full-scale operations. A general outline of conditions employed is given below:

Polypropylene Packings	-- Pall Rings* (5/8, 1, 1-1/2, and 2 inch)
	Flexisaddles** (1 inch)
	Tri-Packs† (2 inch)
	Flexipac Type 2** (a structured packing)
Liquid Loading (L_v)	-- 0.6 - 1.38 $m \cdot min^{-1}$ (2 - 4.5 fpm)
Gas Loading (G_v)	-- 4.6 - 50 $m \cdot min^{-1}$ (15 - 165 fpm)
Temperature	-- 10 - 30°C
Compounds	-- tetrachloroethylene
	1,1,1-trichloroethane
	trichloroethylene
	chloroform
	methylene chloride

The study was accomplished in three phases:

1. First, the possible influence of dilute, organic mixtures on the $K_\ell a$ values of each volatile component was investigated to demonstrate that mutual interactions are negligible under the concentration conditions desired for subsequent study. This was necessary to validate the proposed methodology of

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* Norton Chemical Process Products Division

** Koch Engineerng Company, Inc.

† Jaeger Tri-Packs, Inc.

employing mixtures of the five volatile compounds, pre-dissolved in methanol, in all further $K_\ell a$ determinations.

2. Next, the effects of temperature on $K_\ell a$ were investigated over the range from 10°C - 30°C, using 1-inch Pall rings at a fixed combination of air and liquid loadings. The use of simplified, explicit temperature correlations, as well as the use of the Onda correlations, was evaluated as means of quantifying predictions of temperature effects.

3. A comprehensive study of the effects of packing size, type, and liquid and gas loadings on $K_\ell a$ was performed to provide a rigorous test of the Onda correlations. These experiments were performed at 25°C.

B. PROCEDURES

1. Air-Stripping Facility

The facility used in all air-stripping experiments consisted of a packed tower, a liquid distribution and storage system, an air-distribution system and metering controls as shown in Figure 22.

a. Packed Tower

The packed tower, shown in Figure 23, consisted of a 3.05-meter (10-foot) high, 45.7 cm (18-inch) outside diameter (O.D.), 0.635 cm (1/4-inch) walled, Plexiglass column bolted to a 61 cm (24-inch) wide, 56 cm (22-inch) high, 64 cm (25-inch) deep wooden collection box. The collection box was located approximately 0.9 meters (3 feet) above the floor to permit adequate head for liquid to properly drain. The tower was mounted in a steel angle-iron frame, bolted to the floor. The inside diameter of the tower (17.5 inches) exceeded for all packings the 8:1 minimum column-to-packing-diameter ratio recommended to avoid wall channeling (Treybal, 1980).

The packed column was divided into two sections, connected by bolted flanges at the middle to facilitate disassembly. The ends were sealed with circular Plexiglass plates fastened to the flanges. Rubber gaskets were inserted between all flanges to ensure a tight seal.

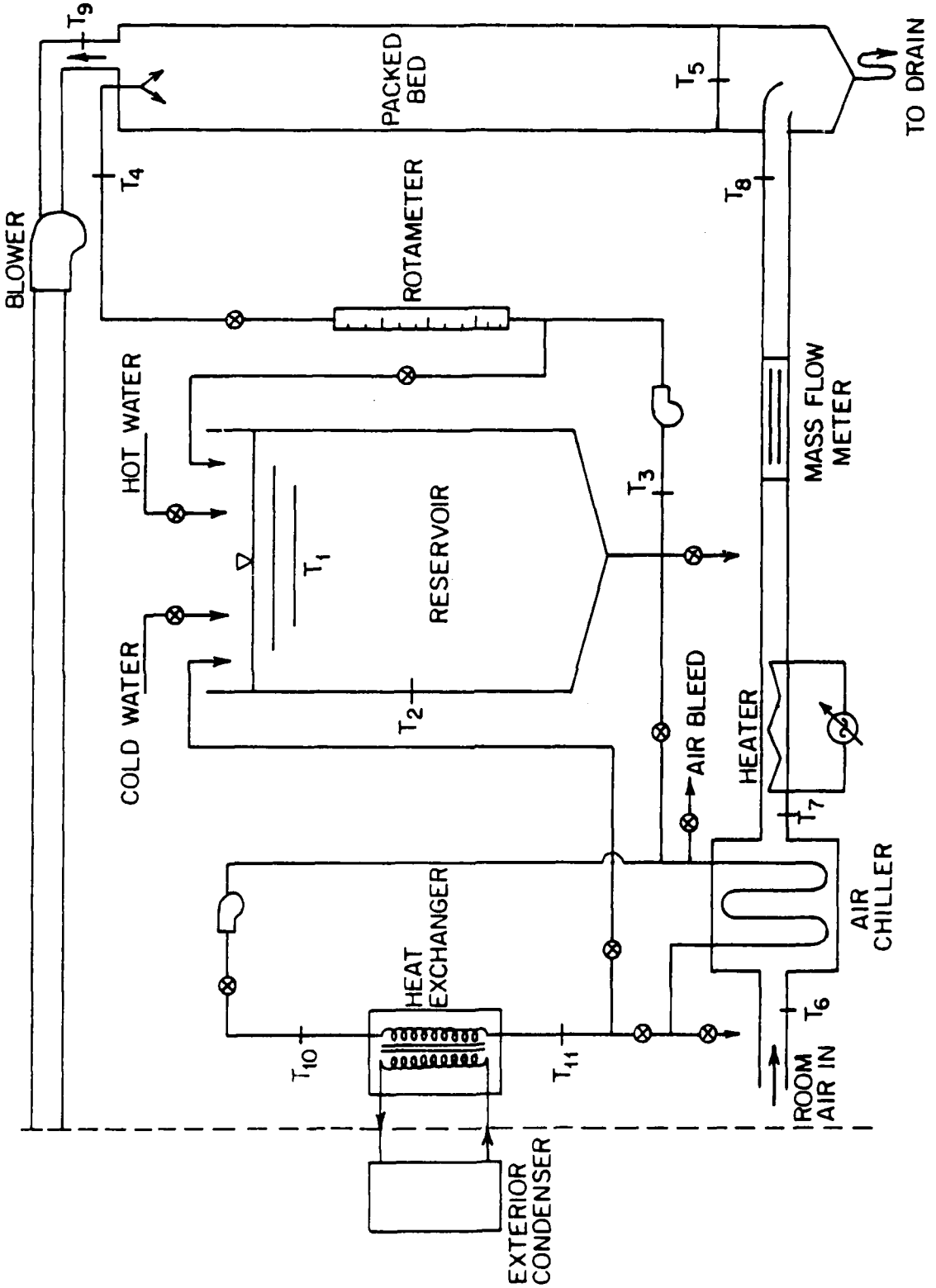

Figure 22. Schematic of Air-Stripping Facility.

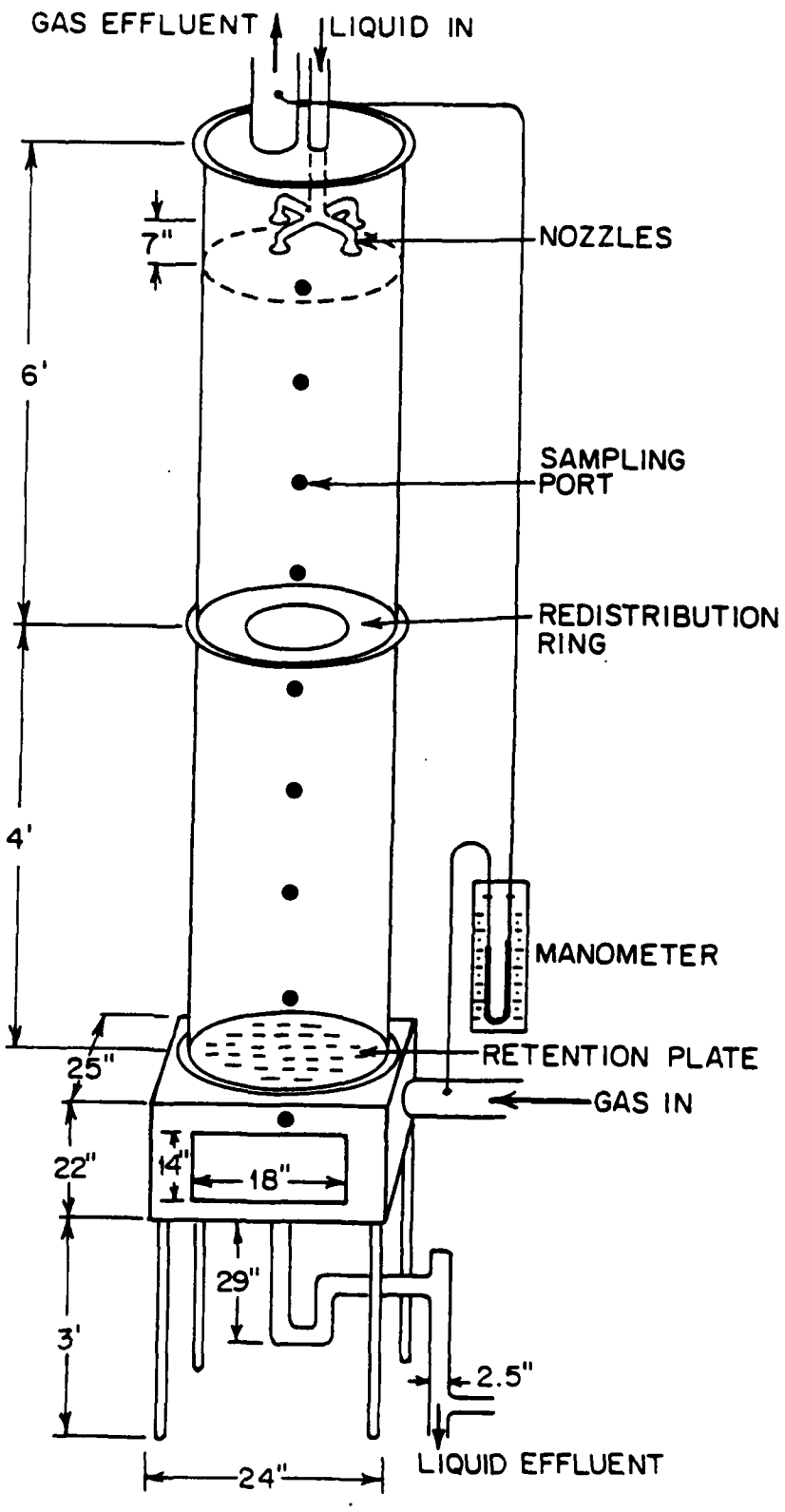

Figure 23. Packed Tower Used for Air-Stripping Studies.

A liquid redistribution ring was originally inserted between the two sections, projecting 4.4 cm (1.75 inches) into the column interior to minimize wall channeling. This ring was only used in studies with 1-inch Pall rings, as it was suspected of causing problems with sample collection. Without the ring, and with a packing depth of 2.4 meters (8 feet), the suggested criterion of 10 column diameters between redistribution points was still satisfied (Treybal, 1980).

The packing material rested on an expanded-metal grating, with 1.3 cm (1/2-inch) diamond openings and 70 percent open area, designed to allow free passage of air and water. The plate was hinged on one side so that it could be dropped to remove the packing.

Nine liquid sampling ports were spaced at 0.3-meter (1-foot) intervals between the top of the packing and the retention plate. The lowest sampling port (Port 0) was located immediately under the retention plate and collected the treated liquid effluent. The highest sampling port (Port 8) rested directly on top of the packing and collected the liquid influent. These ports consisted of 0.635 cm (1/4-inch) Tygon® tubing attached to 0.95 cm (3/8-inch) O.D. rigid plastic tubes approximately 23 cm (9 inches) long, cut lengthwise to form troughs near the inner end, as shown in Figure 24. The plastic tubes projected approximately 15 cm (6 inches) into the packing at a sufficient angle to maintain a steady liquid stream. The liquid flow was controlled by an adjustable clamp at the end of the Tygon® tubing.

b. Liquid Storage and Distribution

The liquid distribution and storage system consisted of a storage reservoir, a pump, a rotameter, and a bank of distributor nozzles. The entire system was designed to accommodate a range of liquid loading conditions likely to be encountered in actual design situations.

A 6400-liter (1700-gallon) stainless-steel cylindrical tank, covered with polyethylene sheeting, was used as a reservoir for the tower influent. A sight gauge on the side of the tank, marked in gallons, was used to calibrate the rotameter and to monitor liquid depth in the tank.

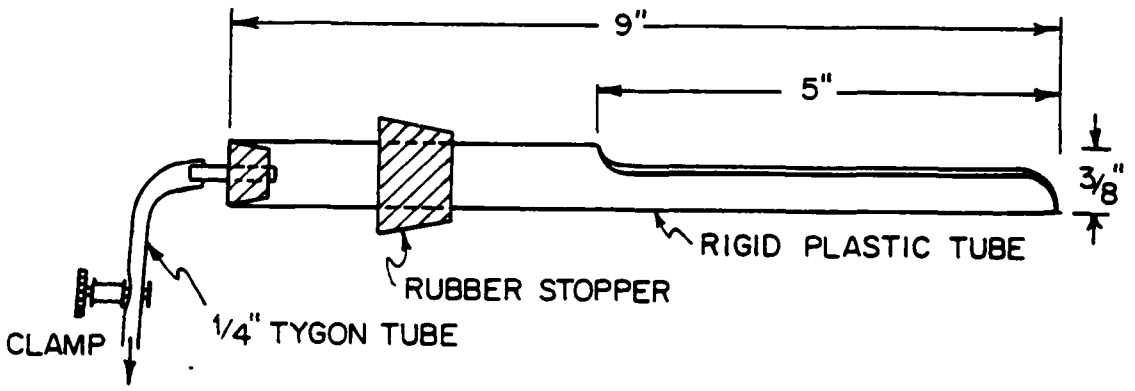

Figure 24. Detail of Sampling Port.

A 7.5 hp flexibly coupled, bronze-fitted centrifugal pump (Armstrong Pumps, Inc. Model 4030) delivered water from the reservoir to the distribution nozzles at the top of the column. The pump was also used to recycle-mix the liquid in the reservoir prior to commencing any experiment, to ensure uniform concentration and temperature. The main distribution and recycle lines were all 5 cm (2-inch) PVC pipe.

A rotameter (Brooks Instrument Division) with a dynamic range of about 10:1 and a maximum capacity of 370 $l \cdot min^{-1}$ (98 gpm) was used to measure the liquid flow rate. Liquid flow was controlled with a 5 cm (2-inch) gate valve immediately following the rotameter.

Liquid was distributed over the top of the packed bed through four solid-cone, stainless-steel nozzles (Sprayco, Model 48621319) each capable of delivering 76 $l \cdot min^{-1}$ (20 gpm) at 210 kPa (30 psig) of pressure. The nozzles were designed to distribute liquid evenly over the top of the packing in a cloverleaf pattern.

The effluent drained through a 6.4 cm (2.5-inch) pipe located in the bottom of the collection box, into the building sewer system. The building sewer could handle flow up to about 230 $l \cdot min^{-1}$ (60 gpm) without backing up, thus establishing the maximum allowable flow through the system.

c. Air Distribution

Air flow was supplied by a direct-drive, centrifugal-type exhauster (Buffalo Forge, Model 4.5 E), driven by a 1.5 bhp, 3600 rpm motor with a solid-state variable-speed controller (Accutrol, 100-7300 Series). Maximum air flow was 10 $m^3 \cdot min^{-1}$ (350 scfm) at 30.5 cm (12-inch) SP. The variable-speed controller provided variable voltage and variable frequency, 0-230 Volt output to the three-phase AC motor. The controller provided an output frequency range of 6 to 120 Hz.

Air flow was countercurrent to liquid flow. Air entered through a 15.2 cm (6-inch) aluminum duct inserted at the base of the tower. Air drawn from the room passed through a chilling coil (15.2 cm by 15.2 cm, 9-row by 18-column). An in-duct heating coil controlled by a 60 Hz, 9.5 amp variable transformer (Staco Energy

Products, Model 3PN1520) was used to heat the air to the desired temperature, allowing sensitive air temperature control.

Air flow was measured using a mass-flow meter (Kurtz Instrument Co.), 0-5 Volt DC linear output, equipped with a Model 525 Digital Display (LED) Bench Cabinet. The mass-flow meter had a dynamic range of up to 100:1, an accuracy of 1 percent, and gave flow rate measurements in units corresponding to standard conditions (25°C and 1 atm). The mass-flow meter was unaffected by changes in temperature, pressure or air density, and arrived calibrated from the manufacturer.

A water-filled manometer was used to measure drops in air pressure across the length of the packed column. The manometer was connected to the air ducts at the entrance to and exit from the tower. The pressure differential was measured as the difference in the water level between the two manometer arms.

d. Temperature Monitoring and Control

The pilot-scale stripping unit was designed to operate over a range of liquid and gas temperatures. The facility included a water-chilling system which served a dual purpose. First, recirculation of reservoir water through the heat exchanger of the water-chilling system adjusted the temperature of the reservoir's contents prior to commencing an experimental run; second, circulating the water in a closed loop between the chiller and the heat exchanger serving the air intake system adjusted and controlled the temperature of the influent air during a run.

The chilling system consisted of an outdoor, year-round, air-cooled 7.5-ton condensing unit (McQuay, Model RHP075), an indoor direct-expansion cooler (equivalent to McQuay, Model CDE-107), and a control unit including chiller freeze stat, system thermostat and temperature controller (McQuay, Model RCP). Recirculation of water through the direct-expansion cooler to and from either the reservoir or the air chiller was accomplished with a 1/3 bhp centrifugal in-line pump (Armstrong Pumps, Inc., Model H52). Recirculation lines were 3.8 cm (1.5-inch) PVC, and mode of recirculation was selected via a number of ball valves. Rate of recirculation was controlled with a gate valve.

Temperatures at 11 points in the stripping facility (designated as T1 through T11 in Figure 22) were monitored using remote temperature probes attached to a single tele-electronic thermometer (YSI, Model 1170). A hand-held thermometer was used to measure influent tap water temperatures. By blending chilled water with warm or cold tap waters, a wide range of water temperatures could be achieved. The massive size of the reservoir provided sufficient heat capacity per transfer surface area that reservoir temperature, once adjusted prior to a run, did not change significantly during the course of a run.

The degree of experimental control varied with the temperature of the run. Some factors were beyond experimental control. For example, controlling the incoming air temperature did not guarantee isothermal operation as temperature changes occurred due to evaporative cooling through the tower and heat transfer with the room air or chilling water during the experiment. Average temperature fluctuations are reported in Table 30. Greater control of gas and liquid temperatures and the least change in temperatures through the column existed for the 30°C runs. Temperature changes in one phase through the column were also beyond experimental control. The water temperature dropped almost 1°C from an initial 10°C as it fell through the column. The average amount of change decreased as the temperature increased until, for the 30°C runs, no detectable change was noted. Gas temperatures also changed the most for the 10°C runs, although the decreasing trend noted for the liquid is not as pronounced due to experimental difficulties when heating the gas was required. The temperature difference between the two phases at the same height in the column also decreased as the temperature increased. The table reveals that the difference between the temperatures at the base of the column (liquid effluent and gas influent) was almost 1.5°C less at 30°C than at 10°C.

For purposes of defining the temperature at which a run was conducted, the liquid temperature data were used. The single temperature reported for a run in later tables and figures is taken as the average of influent and effluent water temperatures at the beginning and end of a run.

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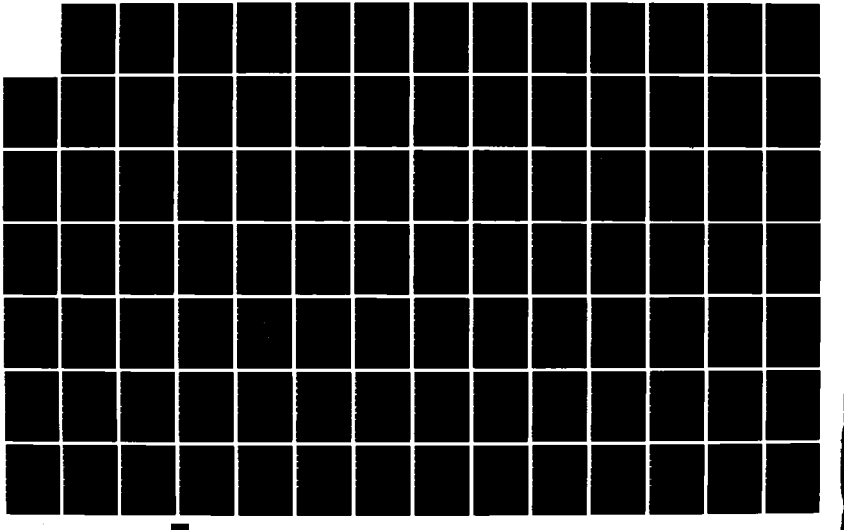

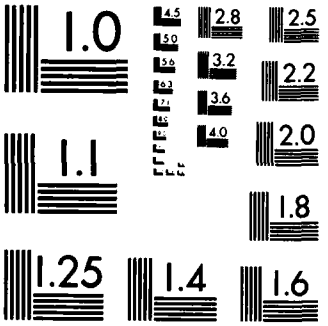

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TABLE 30. AVERAGE TEMPERATURE CHANGES IN THE SYSTEM (°C)

Targeted Run Temp:	10°C	20°C	30°C
$\lvert T_{\ell i} - T_{gi} \rvert_{beg}$	1.0	1.7	0.7
$\lvert T_{\ell i} - T_{gi} \rvert_{end}$	2.0	1.4	0.6
$(T_{gi} - T_{ge})_{beg}$	1.7	1.7	0
$(T_{gi} - T_{ge})_{end}$	2.4	1.8	0.3
$(T_{\ell i} - T_{\ell e})_{beg}$	0.9	0.4	0
$(T_{\ell i} - T_{\ell e})_{end}$	0.8	0.3	0
$(T_{\ell i} - T_{ge})_{end}$	0.7	0.6	0.1
$(T_{gi} - T_{\ell e})_{end}$	2.4	1.2	1.0

Notation: T = temperature (°C)
Subscripts: ℓ = liquid;
g = gas;
i = influent;
e = effluent;
beg = at beginning of run;
end = at end of run.

2. Reagents

Tapwater was used since it was not feasible to distill the large quantity of water needed for stripping experiments. Gas chromatographic analysis showed that the tapwater was relatively free of the volatile organic contaminants studied. The tapwater also had the following characteristics:

Conductivity	360 μmho/cm
pH	7.1
Hardness (as $CaCO_3$)	196 mg/l
Alkalinity (as $CaCO_3$)	90 mg/l

Rather than adding small quantities of the pure volatile organic compounds directly into the reservoir, feed solutions were premixed in stoppered glass containers using a magnetic stirrer to aid dissolution of the hydrophobic compounds. Either tap water at room temperature or methanol was used to dissolve the compounds. The highest purity chemicals commercially available were obtained for the experiments. The compounds studied include tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, chloroform, and methylene chloride. The exact composition of the predissolved feed mixture was varied occasionally among the phases of the air-stripping studies.

The goal was to study stripping of dilute solutions as commonly found in contaminated waters. However, it was necessary to choose concentrations which, after passage through the column, would still produce peaks that were easily read on the gas chromatograph output. For most studies, the approximate concentration of each compound in the reservoir (ignoring volatilization losses) was: 1.5 mg/l for methylene chloride, 1,1,1-trichloroethane, and trichlorothylene; and 3 mg/l for tetrachloroethylene and chloroform. Deviations from these concentration ranges, wherever they occurred, are noted in subsequent sections.

3. Packings

Seven polypropylene packings were used in these studies. Six were randomly dumped packings, whereas one (Flexipac Type 2) was a structured packing. Pertinent data are contained in Table 31.

The tower was packed to a height of 2.44 m (8 feet). To encourage settling, the packing was dumped into the top of the column while water was flowing through the distributor nozzles. Before any stripping runs were made, several tanks of water were pumped over the packing also to promote settling.

4. Column Operation and Sampling

For each experiment, the first step was to fill the storage tank with tap water at the desired temperature. This was accomplished in one of two ways. When the experiment was performed at a temperature above that of the cold tap water, the storage tank was filled with a combination of the hot and cold tap waters. When the water level in the tank was deep enough to prime the 7.5 hp pump, recycle mixing was started to destroy any temperature gradients. While the tank was filling, the organic feed solution was prepared. At approximately 6,000 liters (1600 gallons), the tap water was turned off, and the chemical solution was added to the top of the storage reservoir. Recycle mixing continued for another 25 minutes to ensure uniform chemical composition.

An alternate procedure was followed if the temperature of the tap water exceeded the target temperature. In this case, the cold tap was turned on. When the depth of water in the tank was higher than the 0.33 hp pump, this pump was turned on to circulate tank water through the chiller. The temperature of the water exiting the chiller was adjusted so that the liquid in the storage reservoir would reach the target temperature as quickly as possible. When the sight gauge on the storage tank read 1600 gallons, the tap water was turned off. Chilling continued, if necessary. For the 10°C experiments, it was necessary to chill the water in the storage tank to approximately 9.5°C. Generally, however, little or no temperature change occurred in the tank from beginning to end of an experiment. When the tank was almost at the proper level and temperature, the organic solution was prepared. Once the proper conditions had been established, the chiller was turned off, flow was diverted to the recycle-mix system, and the organic solution was added to the tank. Recycle mixing continued for 25 minutes.

TABLE 31. POLYPROPYLENE PACKING CHARACTERISTICS[a]

Manufacturer	Packing Type	Nominal Diameter, d_p (inches)	d_p (meters)	Surface Area, a_t (ft^{-1})	(m^{-1})	Free Space %	Packing Factor (ft^{-1})	(m^{-1})
Norton	Pall Rings	5/8	0.0159	104	341	87	97	318
		1	0.0254	63	207	90	52	171
		1-1/2	0.0381	39	128	91	40	131
		2	0.0508	31	102	92	24	79
Koch	Flexisaddles	1	0.0254	63	207	91	30	98
Jaeger	Tri-Packs (No. 1)	2	0.0508	42	138	96	15	49
Koch	Flexipac Type 2	7/8[b]	0.0222	75	246	93	22	72

[a] As supplied by manufacturers.

[b] Dimension of one edge of diamond-shaped opening; also corresponds closely to size of Pall ring which would yield equivalent dry surface area per unit packed volume.

During the recycle-mix period, the air temperature entering the column was adjusted to approximately the influent liquid temperature. Ambient air temperature was adequate for 25°C experiments, but other experiments required heating and/or cooling of the incoming air. For 30°C experiments, while the liquid in the storage rank was mixed, the heater was turned on and adjusted to yield air entering the column at approximately 30°C. The 10, 15, and 20°C experiments required more manipulation of the incoming air to achieve the desired temperature. By engaging a closed-loop distribution system, water circulating through the liquid and air chilling units lowered the temperature of the air entering the column to the target temperature. In some cases, higher precision resulted from chilling the air below the target temperature and then reheating the air to the desired temperature.

When the tank was thoroughy mixed and the air temperature adjusted, the air-stripping experiment could begin. Flow from the tank was diverted from the recycle loop to flow through the rotometer and packed column. Liquid and gas flow rates were adjusted, and water temperatures were monitored at the tank exit, column entrance, and column exit to check for isothermal operation. Generally, equilibrium was established in less than 1 minute, although the 10°C experiments required that several hundred gallons passed through the column before thermal conditions stabilized. The column was now ready for a run to begin. A run consisted of recording column conditions and collecting the samples necessary to make one $K_{\ell}a$ determination for each compound.

The following temperatures and flow rates were recorded at the beginning and end of each run:

- water temperatures exiting the tank, entering the column, and leaving the column;
- air temperatures entering and leaving the column;
- liquid flow rate; and
- gas flow rate.

Eleven 25 ml samples were collected beginning with an influent sample (Port 8), followed by an effluent sample (Port 0).

Proceeding up the column, samples were collected at each port (1 through 7) ending with final samples of the influent (Port 8) and effluent (Port 0). Replicate samples of the influent and effluent taken at the beginning and end of the run were used to establish that the column was operating under steady-state conditions.

Before each sample was obtained, liquid in the sampling port was wasted to clear out any liquid left from a previous run. Samples were collected in a 25 ml graduated cylinder and then quickly, but carefully, poured into 120 ml serum bottles. These bottles were immediately sealed with Teflon®-lined rubber septa and aluminum crimp caps. The graduated cylinder was flushed with the effluent prior to sampling the effluent port to avoid contamination from any residual liquid of higher concentration. To minimize volatilization losses, every effort was made to avoid agitation and minimize contact with room air at all points during sample collection.

At the end of the sampling period, temperatures and flow rates were recorded as at the beginning of the run. Minor adjustments were made, as necessary, before the next run. Normally three runs were obtained from one tank of water. Only two runs were obtained during 10°C experiments.

At the end of all runs from one tank, the samples were equilibrated at room temperature and shaken 15 minutes on a wrist-action shaker prior to analysis using headspace chromatography.

5. Criteria for Accepting a Run

The most effective way to control the quality of a stripping run is by establishing criteria limits for accepting a run. The criteria should not eliminate the majority of runs. On the other hand, the criteria should demand the elimination of poorer runs. Based on equipment limitations and on the precision which is achievable, a set of criteria was selected for the various operational parameters. A run which exceeded any of the criteria listed below was rejected.

a. A change in liquid flow rate of 2 $l \cdot min^{-1}$ (0.5 gpm) during a run.

b. A change in gas flow rate of 0.1 $m^3 \cdot min^{-1}$ (4 scfm) over the length of a run.

c. A difference of 0.5°C in water temperature at the beginning and end of a run.

d. A difference between the entering liquid and entering gas temperatures at either the beginning or end of a run of 3.4°C.

e. A difference of 10 percent between replicate influent (Port 8) or effluent (Port 0) samples taken at the start and end of a run.

If a given parameter varies by more than the specified criteria the run is rejected on the basis that operating conditions were unacceptably variable. If the deviations in replicates taken at Port 8 are beyond the criteria limits, the run is rejected on the basis that the influent composition was probably variable due to poor tank mixing. If the replicates at Port 0 differ by more than the criteria limits, it is likely that steady operating conditions have not been achieved in the tower, and therefore the run is rejected.

6. Data Analysis

For a packed tower with liquid sampling ports at various heights from the base of the tower, the concentration of a volatile substance remaining at height z, C_z, is given by the following version of Equation (8)

$$\frac{C_z}{C_e} = \frac{\exp\left[\frac{zA_x}{L}\left(1 - \frac{LRT_g}{GH}\right) K_\ell a\right] - \frac{LRT_g}{GH}}{1 - \frac{LRT_g}{GH}} \qquad (102)$$

where:

C_e = effluent concentration of volatile solute.

Rearranging gives

$$\ln\left[\frac{C_z}{C_e}\left(1 - \frac{LRT_g}{GH}\right) + \frac{LRT_g}{GH}\right] = \frac{zA_x}{L}\left(1 - \frac{LRT_g}{GH}\right) K_\ell a \; . \qquad (103)$$

If C_z data are taken at various heights, z, under steady-state conditions, a plot of the left side of Equation (103) vs.

$(zA_x/L)(1-LRT_g/GH)$ should yield a straight line of slope $K_\ell a$. A representative plot of stripping data is depicted in Figure 25. Analysis of stripping column data requires values of Henry's constant (H). For this purpose, the temperature regression equations provided by the EPICS results (Table 10) were employed.

It should be additionally noted that T_g (the temperature at which the volumetric gas flow rate G is referenced) was 298°C in all cases, since the digital display of the mass flow meter provided a direct readout referenced to 25°C, regardless of the actual air temperature.

In conducting an experiment, it is important to determine the degree to which the various operational parameters affect the quantity being measured. A sensitivity analysis was performed to determine which parameters are most influential in affecting the measurement of $K_\ell a$ via the regression plot technique.

Theoretical data were generated, using calculated concentrations at the various ports to give a perfect line (i.e., $r^2 = 1.00$) for a $K_\ell a$ plot similar to Figure 25. The various system parameters [temperature, T; liquid rate, L; gas rate, G; influent Port, 8; effluent Port, 0] were then allowed to deviate--one at a time--from those employed in deriving the "perfect" data. Table 32 shows how much the $K_\ell a$ value from data analysis deviated from the actual value used to generate the perfect data. This table indicates that small changes in the liquid flow rate produce the most dramatic change in $K_\ell a$. Therefore, it is most critical to accurately measure the liquid rate.

In data analysis for determining $K_\ell a$, a fairly complex expression is calculated to yield an ordinate value, and another rather complicated function is calculated to obtain an abscissa value [see Equation (103)]. Theoretically, the origin (0,0) should be considered a data point. Gossett (1983) has suggested that an error in measuring the effluent concentration (which is generally subject to the greatest percent error) shifts the data line up or down, but has virtually no effect on the slope if the origin is omitted from regression analysis. Recall that the effluent concentration, C_e appears in the function,

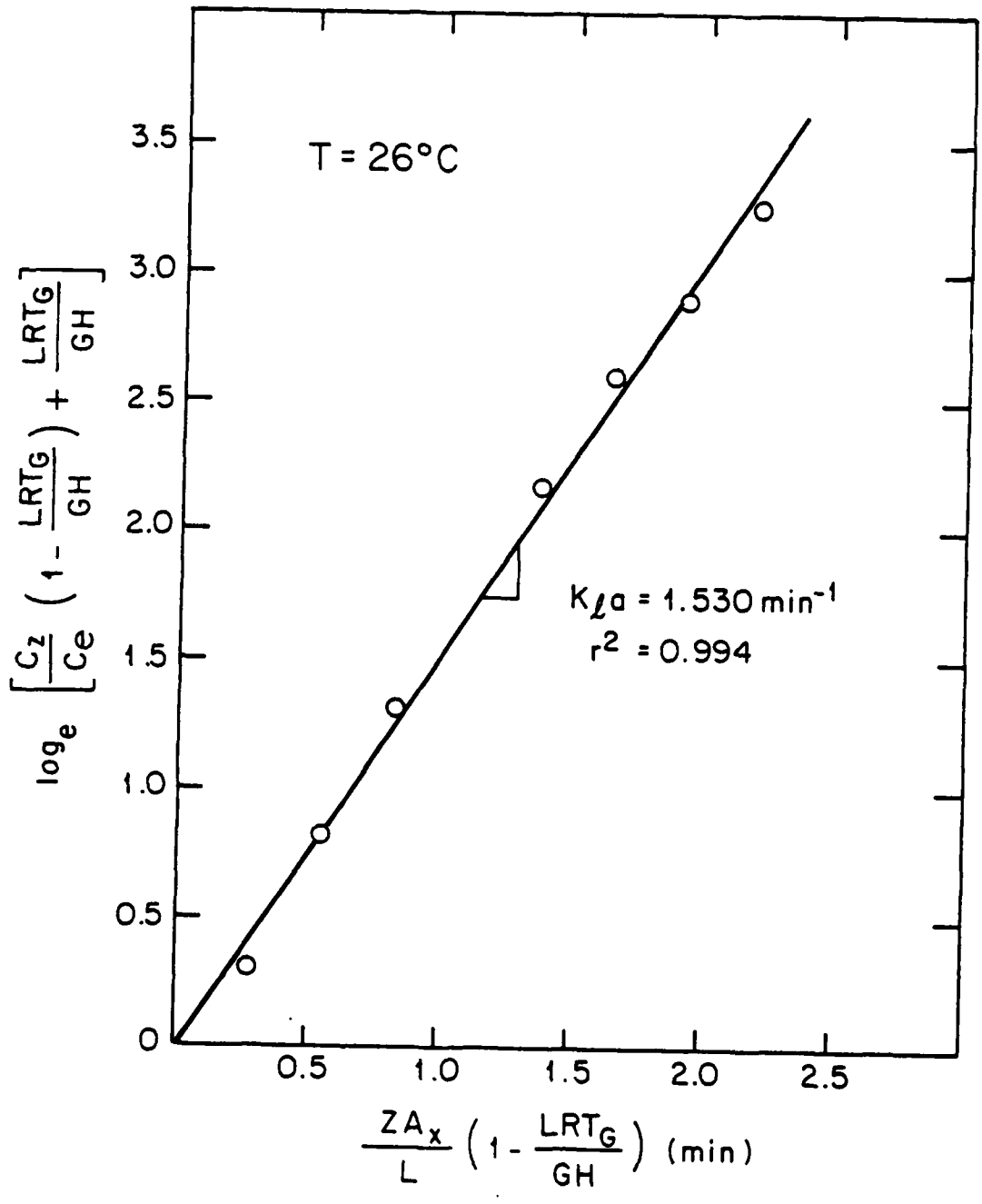

Figure 25. Sample Data Plot from Packed-Tower Studies with 1,1,1-Trichloroethane.

Liquid Loading = 0.92 m/min
Gas Loading = 7.30 m/min
Packing = 5/8-in Pall Rings

TABLE 32. PERCENT CHANGE IN $K_{\ell}a$ FOR TRICHLOROETHYLENE

Parameter	With 5% Δ in Parameter w/ (0,0)	w/o (0,0)	10% Δ in Parameter w/ (0,0)	w/o (0,0)
Liquid Rate (L)	6.2	6.3	12.4	12.7
Temperature, °C (T)	1.5	1.6	3.5	3.8
Effluent Conc. (0)	1.5	0.5	2.8	1.0
Influent Conc. (8)	1.2	1.4	2.4	3.1
Air Rate (G)	1.1	1.3	2.5	2.7

$$\ln\left[\frac{C_z}{C_e}\left(1 - \frac{LRT_g}{GH}\right) + \frac{LRT_g}{GH}\right],$$

and consequently shows up in the other data points in the plot. Inaccuracies in measuring the effluent concentration would move the remaining points out of line from the origin, causing an erroneous $K_\ell a$ if the origin is retained as a data point.

In Table 32, the percent deviation (% Δ) in $K_\ell a$ has been calculated with and without inclusion of the origin as a data point in the regression analysis. It appears that the deviation in $K_\ell a$ due to errors in measuring the effluent concentration can be almost entirely eliminated if the point (0,0) is not used in evaluating the slope. Therefore, the origin was not considered as a data point for regression purposes.

7. Evaluation of the Onda Correlations

The Onda correlations were evaluated by comparison of predicted $K_\ell a$ values with experimentally determined $K_\ell a$ values. The necessary input parameter values to Equations (44), (45), or (46) were obtained as detailed in Table 33. Liquid-phase diffusivities were obtained using the Wilke-Chang correlation (with X = 2.6) as described earlier in this report, despite the availability of our own measured values. The poor precision of our measured D_ℓ values, coupled with their reliance upon a model for mass loss correlation, lessened our confidence in these data; hence we felt justified in using the Wilke-Chang correlation. Data do not exist for gas-phase diffusivities of most of the compounds studied here. This, plus the relative insensitivity of $K_\ell a$ to D_g for predominantly liquid-phase-controlled systems, supports the use of the Hirschfelder correlation for D_g values.

C. RESULTS AND DISCUSSION

1. Preliminary Studies -- Effect of Organic Mixtures on $K_\ell a$

These studies were designed to evaluate the proposed use of dilute mixtures of the five study compounds (predissolved in methanol) in all further stripping experiments. If $K_\ell a$ values of individual

TABLE 33. INPUT PARAMETER VALUES FOR ONDA CORRELATION

Parameter	Temperature 10°C	15°C	20°C	25°C	30°C
d_p (m)	See Table 31				
a_t (m^{-1})	See Table 31				
L_m ($kg \cdot m^{-2} \cdot s^{-1}$)	Set Experimentally				
G_m ($kg \cdot m^{-2} \cdot s^{-1}$)	Set Experimentally				
μ_ℓ (10^{-3} $kg \cdot m^{-1} \cdot s^{-1}$)	1.307	1.139	1.002	0.890	0.798
ρ_ℓ ($kg \cdot m^{-3}$)	999.7	999.1	998.2	997.0	995.7
ρ_g ($kg \cdot m^{-3}$)	1.248	1.226	1.205	1.185	1.165
μ_g (10^{-5} $kg \cdot m^{-1} \cdot s^{-1}$)	1.76	1.79	1.81	1.84	1.86
σ_c ($kg \cdot s^{-2}$)	0.0281				
σ ($kg \cdot s^{-2}$)	0.0742	0.0735	0.0728	0.0720	0.0712
D_ℓ ($m^2 \cdot s^{-1}$)	Wilke-Chang correlation (Equation 63)				
D_g ($m^2 \cdot s^{-1}$)	Hirschfelder correlation (Appendix B)				
H_c (——)	From EPICS Results (Table 10)				

compounds are unaffected by the mutual presence of methanol and the other volatile compounds, then measurements of $K_\ell a$ for each can be greatly expedited by employing mixtures.

First, mass transfer coefficients were measured for the five compounds separately at one temperature (26°C), liquid flow rate (0.92 $m \cdot min^{-1}$), and gas flow rate (7.3 $m \cdot min^{-1}$), using 5/8-inch (0.0159-meter) polypropylene Pall ring packing. Each compound was dissolved in two 5-liter sealed containers of tapwater mixed on a magnetic stirrer for 2 hours to permit maximum dissolution, before being added to the reservoir. The volume of chemical added to the containers depended on the compound studied. The approximate compound concentrations employed are shown in Table 34. At least five replicate runs were made for each compound.

Results of the "Individual Compound Study" are presented in Table 35. A rather small variation exists in the mean $K_\ell a$ values among the five compounds. The reason for this can be explained in terms of the competing effects of diffusivity and volatility on the mass transfer rate. Based on Henry's constants for a temperature of 26°C, the following order in volatility should exist:

tetra > 1,1,1, > TCE > chlor. > meth. chl.

However, the descending order in diffusivity is:

meth. chl. > chlor. > TCE > 1,1,1, > tetra

Therefore, it may be presumed that the difference between the $K_\ell a$'s for the five compounds is small because diffusivity and volatility trends are opposing, and therefore counteract each other.

With the exception of methylene chloride, the precision of the results is quite good. Mass transfer coefficient measurements were repeated at least five times for each compound. The coefficients of variation for all $K_\ell a$ values (except that of methylene chloride) were less than 5 percent. In addition, the coefficient of determination (r^2) of the linear regression of Equation (103) used in determining $K_\ell a$ was greater than 0.99 for all compounds except methylene chloride and chloroform.

TABLE 34. CONCENTRATIONS USED IN INDIVIDUAL COMPOUND STUDY

Compound	Approx. Influent Concentration (mg/l)
1,1,1-trichloroethane	1.0
tetrachloroethylene	0.2
trichloroethylene	1.0
chloroform	2.0
methylene chloride	0.8

TABLE 35. RESULTS FROM STUDY OF INDIVIDUAL COMPOUNDS[a]

Compound	Mean $K_\ell a$ (min^{-1})	% Coeff. of Var.	r^2 Range	n
1,1,1-trichloroethane	1.484	3.6	0.993-0.995	5
trichloroethylene	1.377	2.5	0.988-0.995	9
tetrachloroethylene	1.208	3.2	0.991-0.997	8
chloroform	1.070	3.0	0.971-0.982	5
methylene chloride	0.826	10.0	0.958-0.962	5

[a] L_v = 0.92 m•min^{-1}; G_v = 7.3 m min^{-1}; T = 26°C; Packing = 5/8-inch Pall rings

The lower r^2, and worse precision, for methylene chloride in comparison with the other four compounds is a trait noticeable in virtually all of our stripping experiments. In many cases experimental conditions were such that the stripping factor was less than one for this compound, meaning that the change in sample concentration between successive ports was small, decreasing precision in $K_\ell a$ determinations. Also, it should be remembered that r^2 is a measure of the combined effects of "goodness of fit" and slope. If two sets of data have identical degrees of scatter about their regression lines -- but one line has a much greater slope than the other -- the line of greater slope will have the higher r^2. Thus, there was a generally observed correlation in these studies between $K_\ell a$ (a measure of slope) and r^2 achieved.

If a compound such as methylene chloride were reacting with the packing material, its concentration profile might differ from that predicted by the stripping model alone, causing r^2 and precision problems. An experiment was performed to determine whether the compounds were reacting with the packing. A 25 ml volume of a mixture of the five compounds, at the concentrations given in Table 34, was added to ten 120 ml serum bottles. Five bottles contained several Pall rings, and the other five did not. The 10 bottles were equilibrated for 30 minutes. This greatly exceeded the maximum period that fluid elements were exposed to the packing during stripping runs. Gas headspace samples (0.5 ml volume) were taken. Sample analysis showed no significant difference (< 3 percent) between the peak heights for bottles with and without Pall rings. Since the gas concentrations reflect the concentration in solution via Henry's constant, the results of this experiment indicate that it is unlikely that compound concentrations would be significantly affected by reaction with the packing during stripping runs.

Mass transfer coefficients were measured next for the five compounds in an aqueous mixture with each compound at the same concentration as in the "Individual Compound Study" to determine whether $K_\ell a$ is affected by the presence of additional organics, all at fairly low concentrations typically encountered in contaminated groundwaters.

The mixed organic solution was dissolved in two 5-liter sealed containers on a magnetic stirrer for 8 hours. Although this mixing period was substantially longer than that required for the "Individual Compound Study," volatilization losses did not appear to be signficantly higher.

The concentrations were chosen to give comparable peak height readings for each compound using the headspace chromatographic technique. This made data gathering less cumbersome. However, due to its low solubility, the concentration of tetrachloroethylene used was 1/4 to 1/10 of the other four compounds. The total organic concentration for the mixture experiments was roughly 5 mg/l.

The results of the mixed organic study, showing $K_\ell a$ measurements, coefficients of variation, and r^2 values are given in Table 36. Eight replicate runs were made. These results are compared with the mass transfer coefficient data for the individual component study in Table 37. A two-tailed t-test considering the single component runs as one class and the five-component mixture runs as a second class showed no significant difference at the 95 percent confidence level.

In a third preliminary experiment, mass transfer coefficients were determined for the five compounds in methanol to ascertain that the mutual presence of additional organics does not affect the transfer rate of the volatile organic compounds during air stripping. Two concentration levels of methanol, 60 and 500 mg/l, were used. The concentrations of the volatile organics were identical to those indicated in Table 34. Before adding the volatile organics to the reservoir, the compounds were added to pure methanol and mixed on a magnetic stirrer for 5 minutes. The compounds dissolved almost immediately upon addition to the methanol. The concentration of methanol remained identical from the influent to effluent port, since methanol is relatively nonvolatile from water.

The results of the methanol study are presented in Table 38. This table indicates that dissolving the organic mixtures in either a low or high concentration of methanol does not significantly (less than 5 percent) affect the mass transfer rate. Therefore, interaction

TABLE 36. RESULTS FROM MIXED ORGANIC STUDY[a]

Compound	Mean $K_\ell a$ (min^{-1})	% Coeff. of Var.	r^2 Range	n
1,1,1-trichloroethane	1.520	2.9	0.990-0.998	8
trichloroethylene	1.391	2.3	0.986-0.995	8
tetrachloroethylene	1.212	4.8	0.990-0.998	8
chloroform	1.109	3.5	0.967-0.989	8
methlyene chloride	0.847	5.6	0.948-0.982	8

[a] L_V = 0.92 m•min^{-1}; G_V = 7.3 m•min^{-1}; T = 26°C; Packing = 5/8-inch Pall rings.

TABLE 37. COMPARISON OF INDIVIDUAL COMPOUND AND MIXTURE STUDIES

Compound	Mean $K_\ell a$ (min^{-1}) In Water	Mean $K_\ell a$ (min^{-1}) In a Mixture	Change from Water
1,1,1-trichloroethane	1.484	1.520	+ 2%
trichloroethylene	1.377	1.391	+ 1%
tetrachloroethylene	1.208	1.212	+ 0.3%
chloroform	1.070	1.109	+ 4%
methylene chloride	0.826	0.847	+ 3%

TABLE 38. RESULTS FROM THE METHANOL STUDY[a]

Compound	"Low" Methanol (60 mg/l)			"High" Methanol (500 mg/l)			% Change ("Low" to "High")
	Mean $K_\ell a$	% Coeff. of Var.	r^2 Range	Mean $K_\ell a$	% Coeff. of Var.	r^2 Range	
1,1,1-trichloroethane	1.509	2.5	0.992-0.997	1.520	2.4	0.992-0.998	+ 0.7%
trichloroethylene	1.392	2.8	0.988-0.998	1.387	1.6	0.986-0.993	- 0.4%
tetrachloroethylene	1.253	2.1	0.988-0.998	1.251	3.0	0.989-0.995	- 1.0%
chloroform	1.070	5.5	0.967-0.993	1.063	4.7	0.970-0.989	- 0.7%
methylene chloride	0.833	9.5	0.931-0.983	0.858	5.8	0.920-0.969	+ 3.0%

[a] L_v = 0.92 m•min^{-1}; G_v = 7.3 m•min^{-1}; T = 26°C; Packing = 5/8-inch Pall rings; n = 5 runs.

among the solutes and methanol must be virtually nonexistent and surface activity effects must be minimal.

Figure 26 compares the results for all the stripping studies performed to measure $K_\ell a$ for the five volatile organic compounds. A statistical analysis of variance considering four separate classes of $K_\ell a$ measurements (individual component, mixture, and the two levels of methanol) found no significant differences between the measured $K_\ell a$'s at a 5 percent level. The fact that the $K_\ell a$'s so not differ between the studies indicates that the compounds do not exhibit surface active or reactive interaction effects at the concentrations used. This supports the use of predissolved mixtures of the volatiles in methanol for all subsequent experiments.

2. Effect of Temperature on $K_\ell a$

Using 1-inch (2.54 cm) polypropylene Pall rings, $K_\ell a$ values were determined for each of the five study compounds at temperatures ranging from 10°C to 30°C, with a liquid loading of 1.36 $m \cdot min^{-1}$, and a gas loading of 10.95 $m \cdot min^{-1}$ (referenced to 25°C, 1 atm). All studies used mixtures of the five volatiles, predissolved in 500 ml of methanol. The approximate reservoir concentrations are shown in Table 39. At least four $K_\ell a$ values were determined within 1.5°C of each target temperature (10, 15, 20, 25, or 30°C) for each compound.

Without exception, mass transfer coefficients increased markedly over the 20°C temperature range examined. Approximate $K_\ell a$'s at 10 and 30°C and the percentage increase in $K_\ell a$ for each compound are presented in Table 40. At every temperature examined, methylene chloride had the lowest mass transfer coefficient, followe' in ascending order by chloroform, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane. The compounds with the lowest mass transfer coefficients exhibited the greatest sensitivity to changes in temperature.

The significant temperature dependency observed for all compounds contradicts Mackay and Leinonen's (1975) assertion that mass transfer coefficients are relatively temperature-insensitive. The

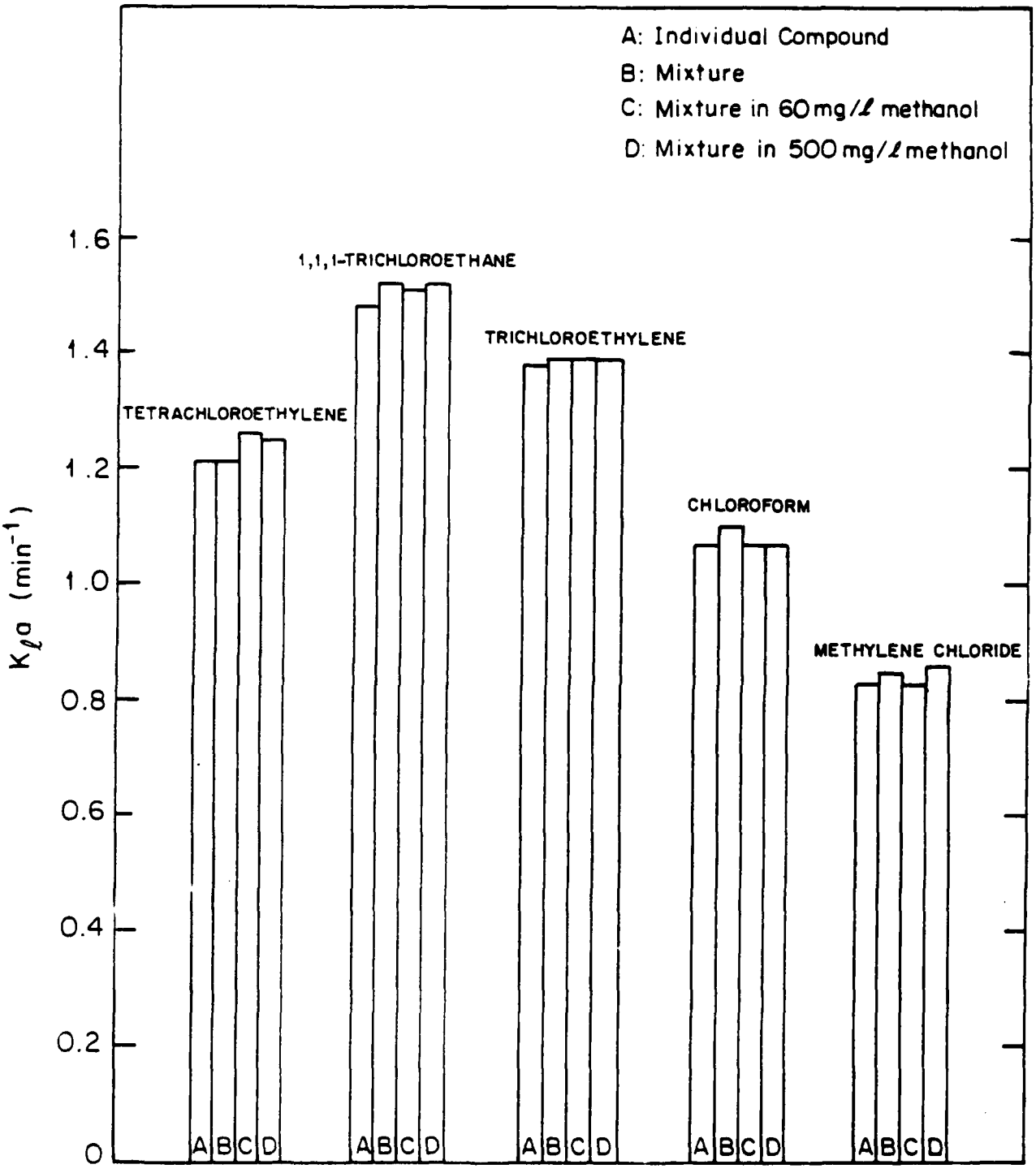

Figure 26. Comparison of Mean $K_\ell a$ Values for All Stripping Studies.

TABLE 39. ORGANIC SOLUTION FOR TEMPERATURE STUDIES

	Volume Added to 500 ml methanol (ml)	Approx. Conc. in Reservoir (mg/l)
tetrachloroethylene	8.0	2.1
1,1,1-trichloroethane	4.8	1.0
trichloroethylene	4.0	1.0
chloroform	8.0	2.0
methylene chloride	3.6	0.8

TABLE 40. CHANGES IN $K_{\ell}a$ FROM 10 TO 30°C.

	Mean $K_{\ell}a$ (min^{-1})		% Increase from 10 - 30°C
	@ ≃ 10°C (n = 6)	@ ≃ 30°C (n = 7)	
tetrachloroethylene	0.90	1.70	89
1,1,1-trichloroethane	1.02	1.81	77
trichloroethylene	0.75	1.56	108
chloroform	0.39	1.10	182
methylene chloride	0.28	0.79	182

slight increase in the overall mass transfer coefficient (K_ℓ) for benzene from 10 - 25°C reported by Mackay and Leinonen could be due to errors in the limited data collected or to differences in the physical properties of the mass transfer systems involved. Evaporative mass transfer is not subject to the high turbulence of a packed tower. Additionally, the volumetric mass transfer coefficient measured for this report ($K_\ell a$) reflects possible temperature-induced changes in the interfacial area, a factor excluded in the overall mass transfer coefficient (K_ℓ) reported by Mackay and Leinonen.

It is interesting to compare the results of this study to Kavanaugh and Trussell's (1981) air-stripping investigation. Their report of a 10 percent decrease in the mass transfer coefficient and a 50 percent decrease in Henry's constant for chloroform as temperature dropped from 20°C to 10°C is substantially smaller than indicated by the results of this research. In this study, the drop from 20 to 10°C resulted in a measured 50 percent decrease in $K_\ell a$ and a 40 percent decrease in the calculated Henry's constant for chloroform.

Since the observed effect of temperature on Henry's constant was similar in the two studies, it would appear that the difference between the $K_\ell a$ results obtained by Kavanaugh and Trussell and the results of this research could be due to differences in percentage of gas-phase resistance between the two studies. (If the effect of temperature on liquid-phase resistance is quantitatively different than the effect of temperature on gas-phase resistance, then the observed effect of temperature on overall resistance ($1/K_\ell a$) would be a function of the percentage gas-phase resistance in any system). Gas flow rate, packing type and size, and gas-to-liquid ratio would influence how strongly temperature affects mass transfer rates, and thus, the efficiency of an air-stripping operation.

The data obtained for each compound from 10°C to 30°C are presented graphically in Figures 27 through 31. The mass transfer coefficients exhibit a positive trend when plotted against temperature in this manner which suggests that a linear expression can correlate mass transfer coefficients with temperature (°K). The resulting linear regressions are presented in Figures 27 through 31. Given that

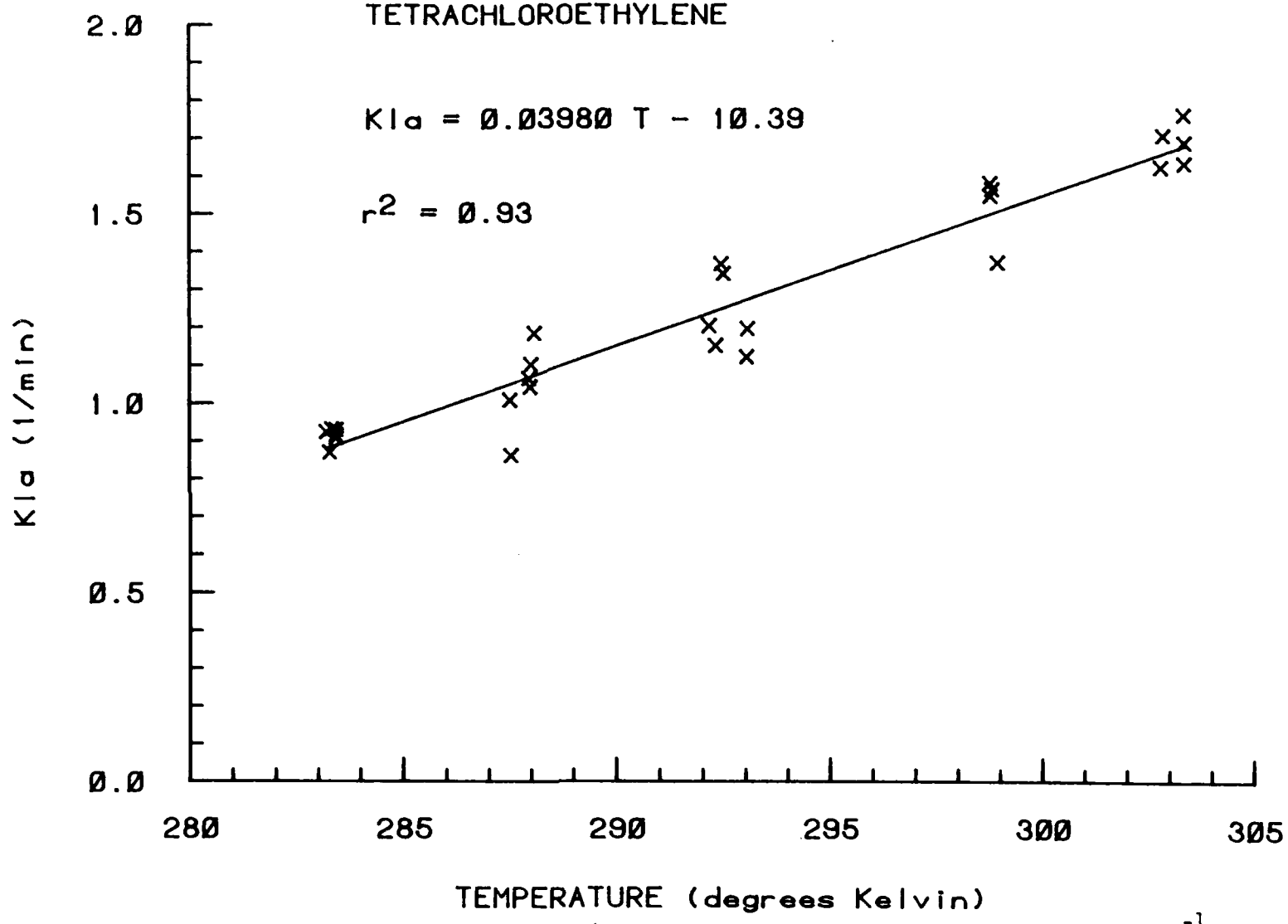

Figure 27. $K_\ell a$ vs Temperature -- Tetrachloroethylene (1-Inch Polypropylene Pall Rings, L_v = 1.36 m·min^{-1}, G_v = 10.95 m·min^{-1}. [Ref: 25°C, 1 atm]).

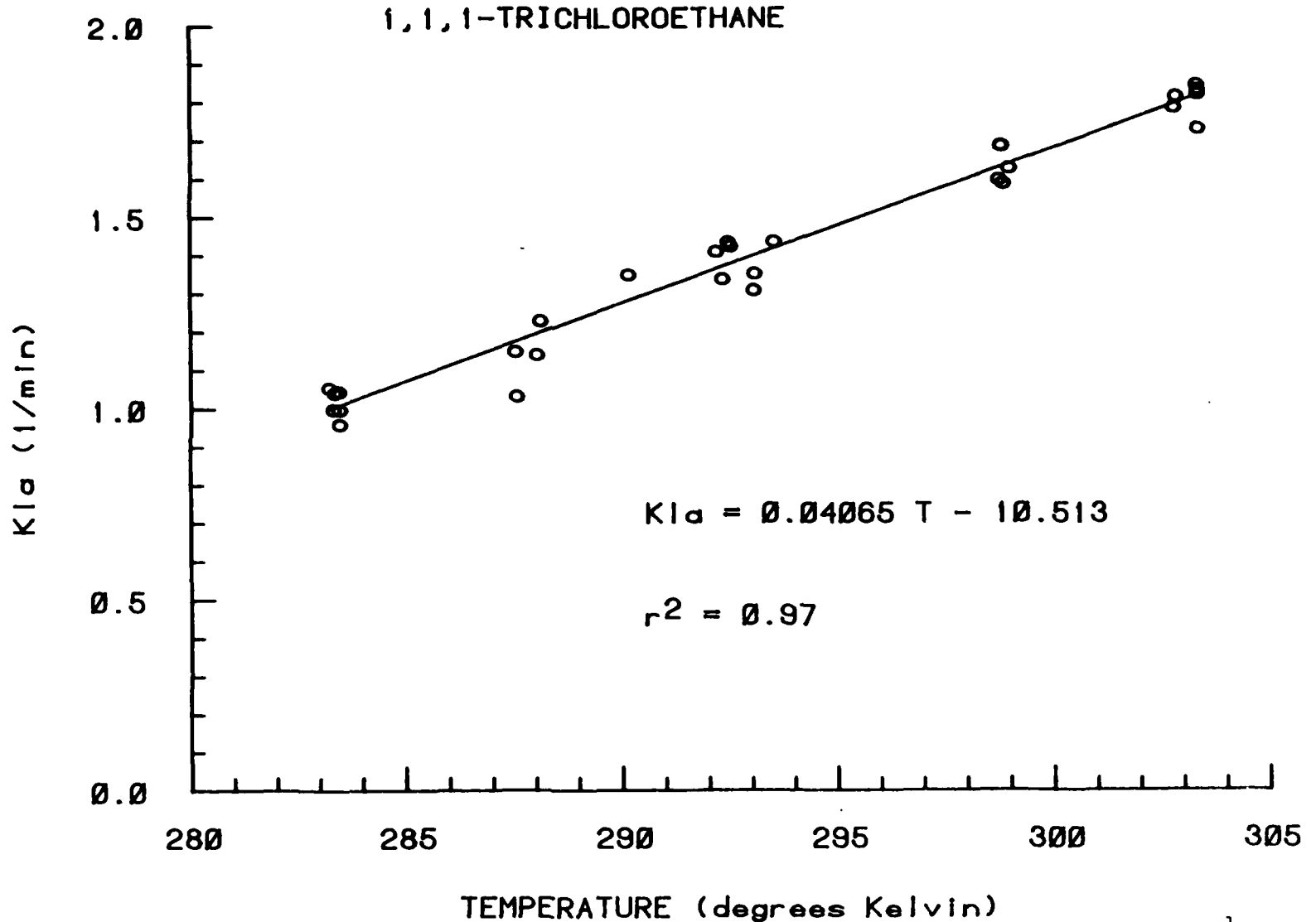

Figure 28. $K_\ell a$ vs Temperature -- 1,1,1-Trichloroethane (1-Inch Polypropylene Pall Rings, L_V = 1.36 m·min^{-1}, G_V = 10.95 m·min^{-1} [Ref: 25°C, 1 atm]).

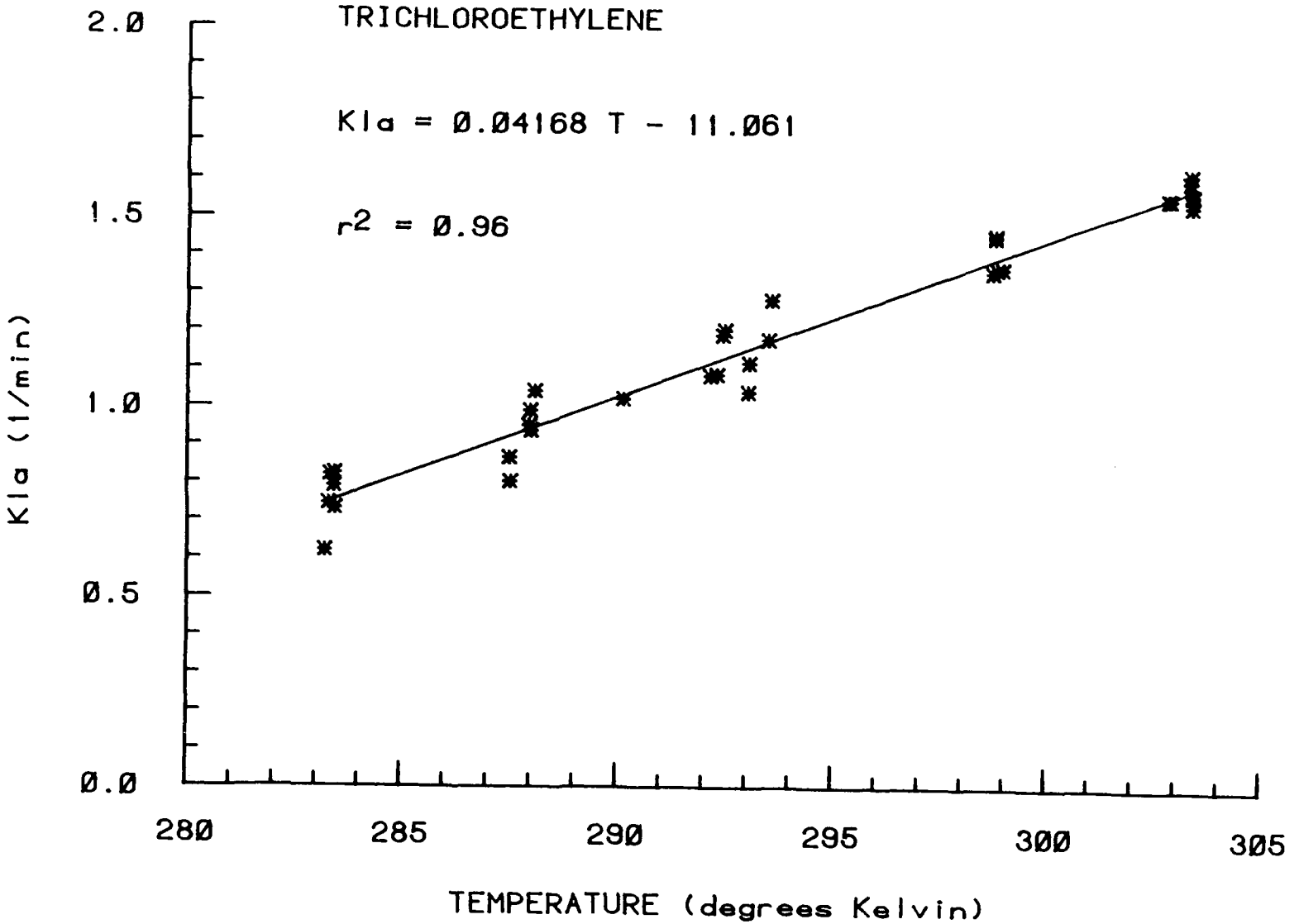

Figure 29. $K_\ell a$ vs Temperature -- Trichloroethylene. (1-Inch Polypropylene Pall Rings, L_v = 1.36 $m \cdot min^{-1}$, G_v = 10.95 $m \cdot min^{-1}$ [Ref: 25°C, 1 atm]).

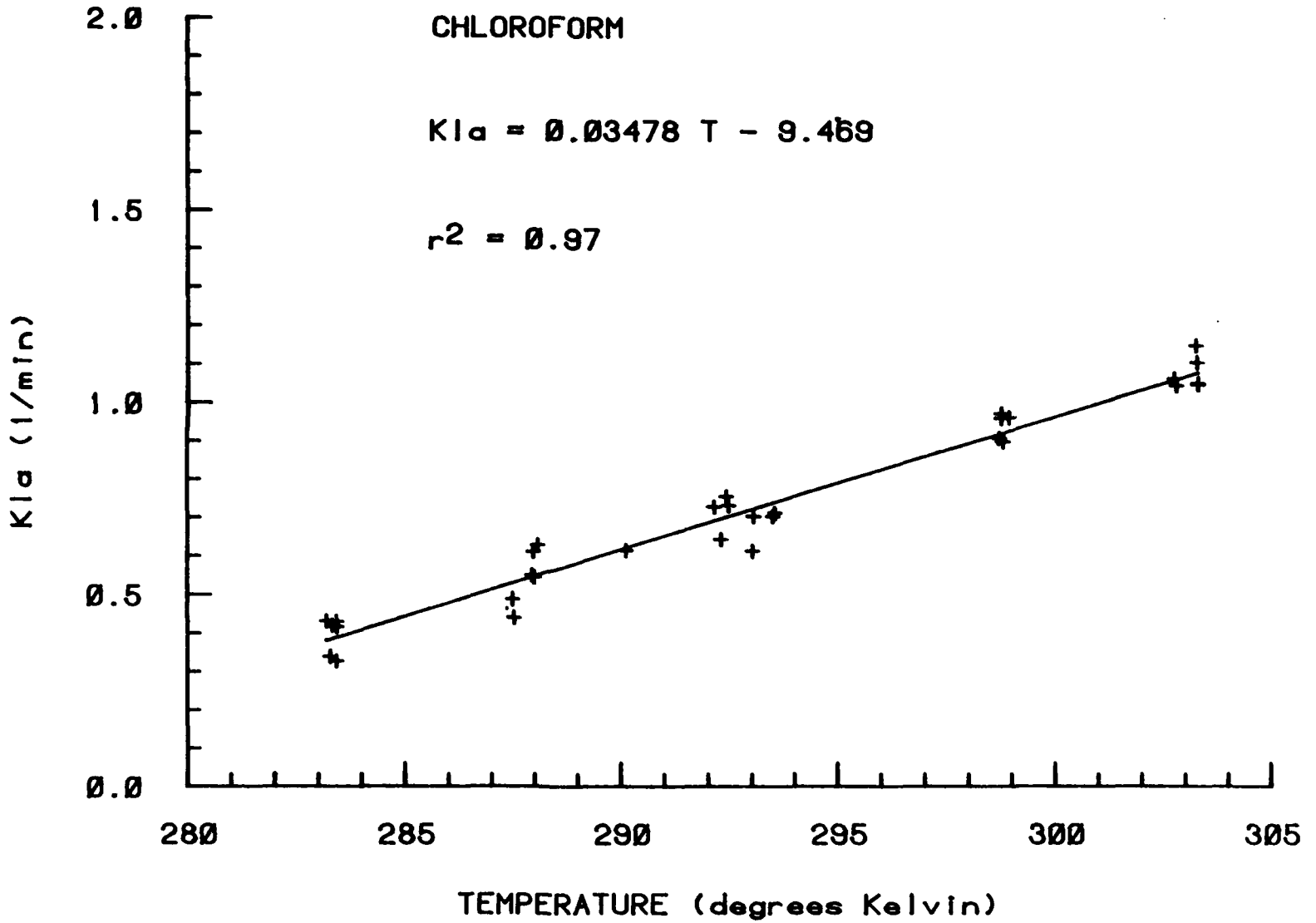

Figure 30. $K_\ell a$ vs Temperature -- Chloroform. (1-Inch Polypropylene Pall Rings, L_V = 1.36 m·min^{-1}, G_V = 10.95 m·min^{-1} [Ref: 25°C, 1 atm]).

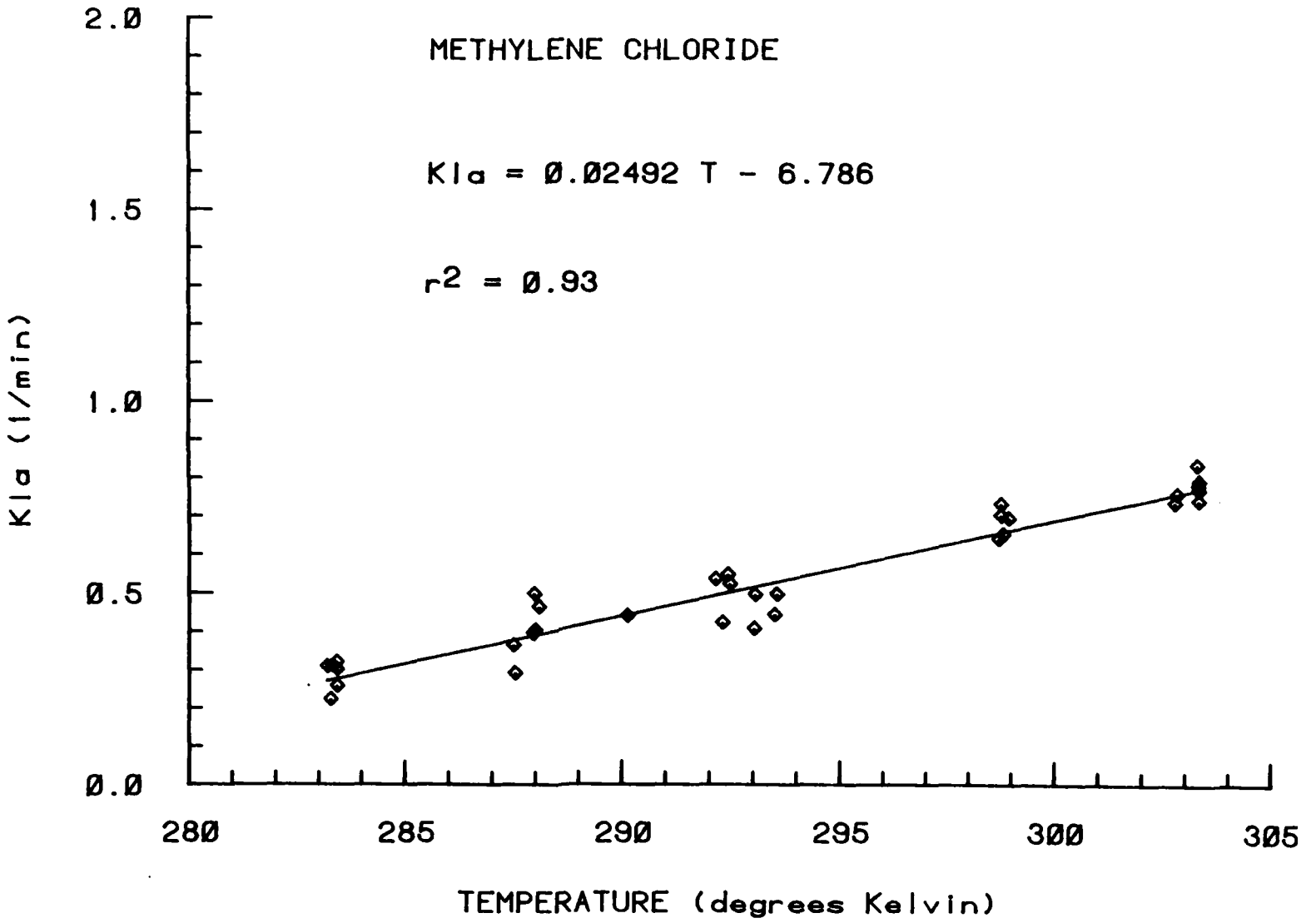

Figure 31. $K_\ell a$ vs Temperature -- Methylene Chloride. (1-Inch Polypropylene Pall Rings, L_v = 1.36 $m \cdot min^{-1}$, G_v = 10.95 $m \cdot min^{-1}$ [Ref: 25°C, 1 atm]).

all coefficients of determination exceed 0.9, this simple relationship would seem adequately to describe changes with temperature for the conditions of this study.

An exponential relationship analogous to those developed by Vivian and King (1964) and Sherwood and Holloway (1940) was derived for each compound (Table 41). This relationship also appears to correlate $K_\ell a$'s to temperature (°C) satisfactorily . The results of this research contradict Sherwood and Holloway's observation that the mass transfer coefficient is greater for compounds with higher diffusivities. As discussed earlier, this could reflect hydrodynamic or volatility differences between their studies and ours, reflecting differences in percentage gas-phase resistance. After all, their correlation is really one for $k_\ell a$, not $K_\ell a$.

The results using an Arrhenius-type dependency, employed successfully by Gossett (1983), are depicted in Table 42. Again, this model expresses the temperature (°K) dependence of the $K_\ell a$'s measured, with all coefficients of determination greater than or equal to 0.9. Trichloroethylene showed a greater sensitivity to temperature than in Gossett's study, reflecting the fact that temperature's effect on mass transfer is related to physical and/or operating characteristics of the system, such as liquid and/or gas loadings, or differences in packing. The discrepancy between the two studies is no doubt a consequence of differences in the influence of gas-phase resistance (and therefore of Henry's constant).

The final model investigated was the simplified Onda correlation for $K_\ell a$:

$$K_\ell a \propto T^{1/2} \mu_\ell^{-4/3} \qquad (104)$$

Regressions using this model, presented in Table 43, appear to fit the data as well as the other models, at least based upon r^2. Note, however, that in some cases a significant intercept ("A" value in the table) is evident, whereas the model predicts none.

The peculiar ability of each of these different models apparently to fit the data is likely a consequence of the modest temperature range of the study.

TABLE 41. EXPONENTIAL CORRELATION OF $K_\ell a$ (min^{-1}) WITH TEMPERATURE (°C)[a].

	r^2
Tetrachloroethylene	
$\ell n\ K_\ell a = -0.422 + 0.0317\ t_c$	0.92
1,1,1-Trichloroethane	
$\ell n\ K_\ell a = -0.277 + 0.0295\ t_c$	0.96
Trichloroethylene	
$\ell n\ K_\ell a = -0.634 + 0.0370\ t_c$	0.93
Chloroform	
$\ell n\ K_\ell a = -1.394 + 0.0502\ t_c$	0.94
Methylene Chloride	
$\ell n\ K_\ell a = -1.732 + 0.0502\ t_c$	0.90

[a] 1-inch polypropylene Pall rings; L_v = 1.36 $m \cdot min^{-1}$; G_v = 10.95 $m \cdot min^{-1}$ (ref: 25°C, 1 atm)

TABLE 42. ARRHENIUS-TYPE CORRELATION OF $K_\ell a$ (min^{-1}) WITH TEMPERATURE (°K).[a]

	r^2
Tetrachloroethylene	
$\ell n\ K_\ell a = 9.50 - 2721/T$	0.92
1,1,1-Trichloroethane	
$\ell n\ K_\ell a = 8.967 - 2534/T$	0.96
Trichloroethylene	
$\ell n\ K_\ell a = 10.98 - 3184/T$	0.93
Chloroform	
$\ell n\ K_\ell a = 14.40 - 4331/T$	0.94
Methylene Chloride	
$\ell n\ K_\ell a = 13.94 - 4296/T$	0.90

[a] 1-inch polypropylene Pall rings; $L_v = 1.36\ m \cdot min^{-1}$; $G_v = 10.95\ m \cdot min^{-1}$ (ref: 25°C, 1 atm).

TABLE 43. SIMPLIFIED ONDA CORRELATION FOR TEMPERATURE EFFECTS.[a]

$$K_\ell a = A + B\, T^{1/2}\, \mu_\ell^{-4/3}$$

$\min^{-1}$ °K cP

Compound	A	B	r^2
tetrachloroethylene	0.095	0.0677	0.93
1,1,1-trichloroethane	0.207	0.0686	0.97
trichloroethylene	-0.056	0.0695	0.95
chloroform	-0.284	0.0579	0.96
methylene chloride	-0.206	0.0415	0.93

[a] 1-inch polypropylene Pall rings; L_v = 1.36 m·$\min^{-1}$; G_v = 10.95 m $\min^{-1}$ (ref: 25°C, 1 atm).

It was orginally (and naively) hoped that temperature relationships derived from this research would generally apply to estimating temperature-induced changes in efficiency for air-stripping facilities. However, further examination of the complexities of mass transfer in such systems has served to demonstrate how unrealistic this expectation was, at least for systems possessing significant gas-phase resistance. Comparison of these results to those from other research indicates that the correlations are of limited utility, in that they are only applicable to the operating conditions (L, G, and packing) used to generate them.

From a theoretical perspective, none of the simplistic correlations can accurately reflect temperature-induced changes in $K_\ell a$. Recall the additivity of resistances:

$$\frac{1}{K_\ell a} = \frac{1}{k_\ell a} + \frac{1}{H_c k_g a} \qquad (105)$$

Any simple linear or log-linear realtionship cannot be valid over broad temperature ranges or over a variety of loading and packing conditions, as correlations of this form do not reflect the changing importance of k_ℓ, k_g, and H_c in controlling mass transfer. Only in cases where percentage gas-phase resistance is negligible (or constant) can there be the realistic expectation of simplistic, explicit modelling of temperature effects.

The more generally applicable approach would seem to be the use of temperature-corrected parameters (i.e., viscosities, diffusivities, Henry's constant, etc.) in conjunction with the two-resistance model and Onda's correlations. $K_\ell a$ estimates using the Onda correlations are contained in Table 44, along with mean, measured values at 10°, 20°, and 30°C for the conditions employed in this present phase of study. Examination of the last column shows that the Onda correlation predicts accurate $K_\ell a$ values for the more volatile compounds, but is seriously in error for chloroform and methylene chloride. Note that the agreement with measured values appears to be inversely related to the percentage gas-phase resistance.

Due to the complexity of the equations involved, no attempt was made to modify specific components of the expressions for k_ℓ and

TABLE 44. COMPARISON OF PREDICTED AND MEASURED $K_{\ell}a$ VALUES.

(1-inch polypropylene Pall rings; L_v = 1.36 m·min^{-1};

G_v = 10.95 m·min^{-1} [ref: 25°C, 1 atm]).

Compound	Temp.	Mean Meas. $K_{\ell}a$ (min^{-1})	Onda Predictions $K_{\ell}a$ (min^{-1})	Onda Predictions % R_g[a]	Onda Predictions % D[b]
tetrachloroethylene	10°C	0.90	0.890	8.1	- 1.1
	20°C	1.25	1.33	6.4	+ 6.4
	30°C	1.70	1.87	5.0	+10.0
1,1,1-trichloroethane	10°C	1.02	0.925	7.0	- 9.3
	20°C	1.40	1.37	6.1	- 2.1
	30°C	1.81	1.92	5.2	+ 6.1
trichloroethylene	10°C	0.75	0.890	12.5	+18.7
	20°C	1.15	1.34	10.2	+16.5
	30°C	1.56	1.90	8.2	+21.8
chloroform	10°C	0.39	0.821	23.2	+110
	20°C	0.71	1.24	20.8	+74.6
	30°C	1.10	1.77	18.3	+60.9
methylene chloride	10°C	0.28	0.801	30.3	+186
	20°C	0.48	1.22	27.4	+154
	30°C	0.79	1.76	24.4	+123

[a] percent gas-phase resistance, as estimated by Onda correlations.

[b] $\left(\frac{K_{\ell}a\ [\text{Onda}]}{K_{\ell}a\ [\text{Meas.}]} - 1 \right) 100$

k_g. (There is little support for changes based solely upon data limited to one packing, one gas loading, and one liquid loading.) However, a simplistic approach to modification of the correlations can be used: That is, alteration of the Onda-predicted $k_\ell a$ and $k_g a$ values by constant factors λ and ϕ, respectively. This is tantamount to changing the constants (0.0051 and 5.23) appearing in front of the dimensionless factors in the k_ℓ and k_g expressions [Equations (44) and (45)].

Suppose that the "true" mass transfer coefficient, $(K_\ell a)_*$, differs from the Onda-predicted $(K_\ell a)_o$ because of errors in the aforementioned constants. In this case,

$$\frac{1}{(K_\ell a)_o} = \frac{1}{(k_\ell a)_o} + \frac{1}{(k_g a\, H_c)_o} \tag{106}$$

whereas:

$$\frac{1}{(K_\ell a)_*} = \frac{1}{\lambda(k_\ell a)_o} + \frac{1}{\phi(k_g a\, H_c)_o} \tag{107}$$

where:

$\frac{1}{(k_\ell a)_o}$, $\frac{1}{(k_g a\, H_c)_o}$ = resistances in the liquid and gas phases, respectively, as predicted by the Onda correlations;

λ, ϕ = constants required to correct the Onda-predicted $k_\ell a$ and $k_g a$ expressions, respectively.

We may write:

$$\frac{1}{(K_\ell a)_*} - \frac{1}{(K_\ell a)_o} = \frac{1}{\lambda(k_\ell a)_o} - \frac{1}{(k_\ell a)_o} + \frac{1}{\phi(k_g a\, H_c)_o} - \frac{1}{(k_g a\, H_c)_o}$$

$$= \left(\frac{1}{\lambda} - 1\right) \frac{1}{(k_\ell a)_o} + \left(\frac{1}{\phi} - 1\right) \frac{1}{(k_g a\, H_c)_o} \tag{108}$$

Therefore,

$$\frac{(K_\ell a)_o}{(K_\ell a)_*} - 1 = \left(\frac{1}{\lambda} - 1\right) \frac{(K_\ell a)_o}{(k_\ell a)_o} + \left(\frac{1}{\phi} - 1\right) \frac{(K_\ell a)_o}{(k_g a\, H_c)_o} \tag{109}$$

If we assume that measured values $(K_\ell a)_m$ approximate true values $(K_\ell a)_*$, then the left-hand side of Equation (109) is simply the fractional difference between Onda and measured $K_\ell a$ values. Hence,

$$\% D = \left(\frac{1}{\lambda} - 1\right) (\% R_\ell)_o + \left(\frac{1}{\phi} - 1\right) (\% R_g)_o \,. \tag{110}$$

where:

% D = percentage difference of $(K_\ell a)_o$ from $(K_\ell a)_m$;

$(\% R_\ell)_o$ = percent liquid-phase control as predicted by Onda

$= (K_\ell a)_o / (k_\ell a)_o$;

$(\% R_g)_o$ = percent gas-phase control as predicted by Onda

$= (K_\ell a)_o / (k_g a\ H_c)_o$.

Realizing that $(\% R_\ell)_o = 100 - (\% R_g)_o$, then (by substitution):

$$\% D = 100 \left(\frac{1}{\lambda} - 1\right) + (\% R_g)_o \left[\frac{1}{\phi} - \frac{1}{\lambda}\right] . \qquad (111)$$

A plot of % D vs $(\% R_g)_o$ would yield a straight line if the only modifications needed in the Onda correlations are simple changes of constants in front of the $k_\ell a$ and $k_g a$ expressions. From the intercept and slope of such a plot, the modification factors λ and ϕ can be determined.

A plot of Equation (111) for the data of Table 44 is shown in Figure 32. The straight line in the figure was obtained by linear regression of the data, yielding a slope of 6.88 and intercept of -46.1, with a coefficient of determination (r^2) of 0.94. These values result in $\lambda = 1.85$, $\phi = 0.135$. This suggests that a better fit of the $(K_\ell a)_m$ data could be obtained by increasing the $(k_\ell a)_o$ value by 85 percent, while decreasing the $(k_g a\ H_c)_o$ value by 87 percent. Effectively, the gas-phase resistance would be increased 7.4 times, while the liquid-phase resistance would be nearly halved. Examples of the data fits so-obtained are contained in Figures 33 and 34 for the most volatile (tetrachloroethylene) and least volatile (methylene chloride) of the compounds, respectively.

A few points should be emphasized. First, though the r^2 value for the line in Figure 32 is impressive, careful examination will show the data trend to be definitely nonlinear. This indicates more modifications than simple changing of front-constants in the Onda expressions are needed. Secondly, it remains to be seen whether λ and ϕ remain constant throughout studies which encompass a variety of packings. If so, this would be a persuasive argument for modifying

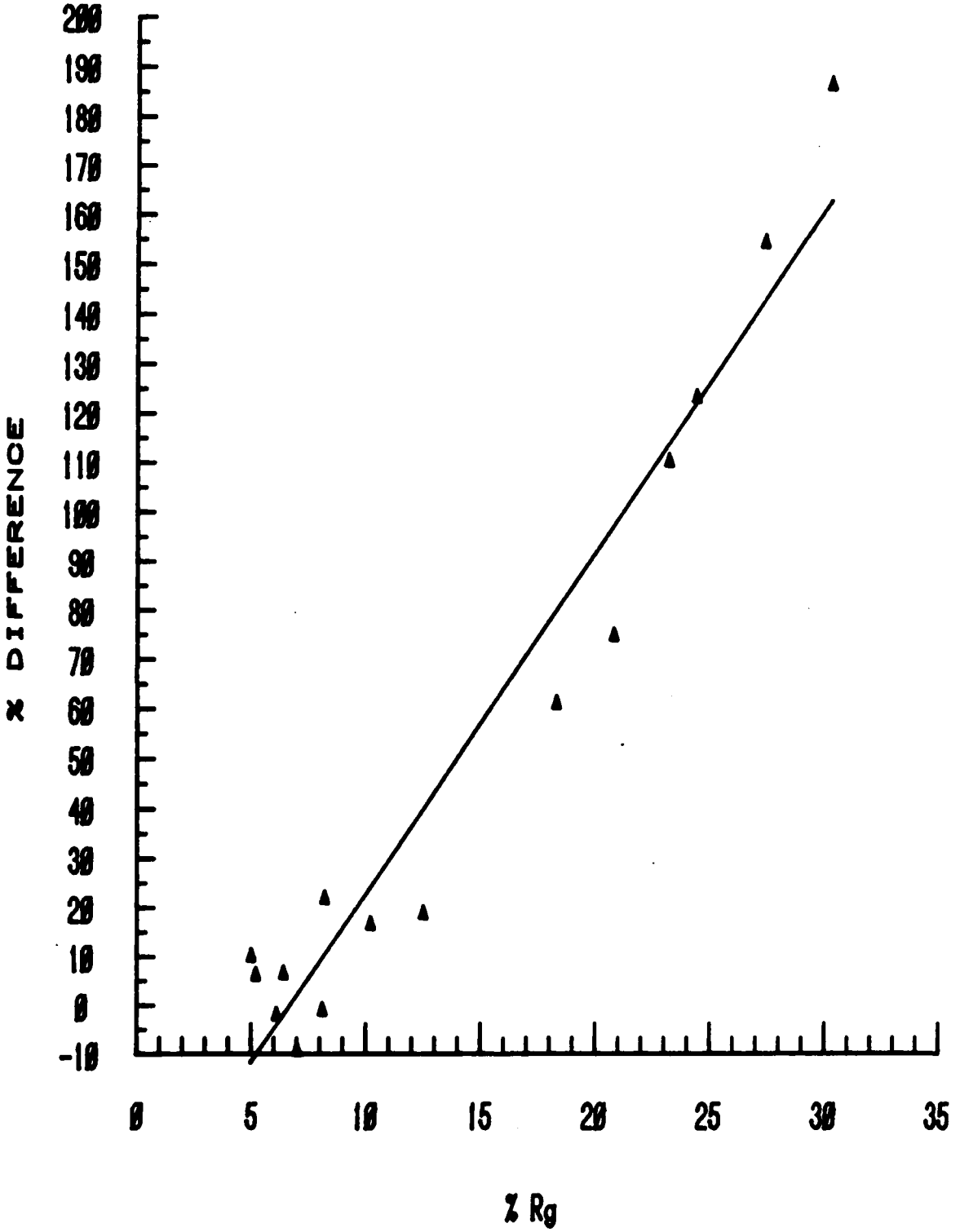

Figure 32. Percent Difference Between Onda-Predicted and Measured $K_{\ell}a$ versus Onda-Predicted Percent Gas-Phase Resistance. Equation for Regression Line is % D = -46.1 + 6.88 $(\% R_g)_o$ (1-Inch Pall Rings, L_v = 1.36 m·min^{-1}, G_v = 10.95 m·min^{-1} [Ref: 25°C, 1 atm]).

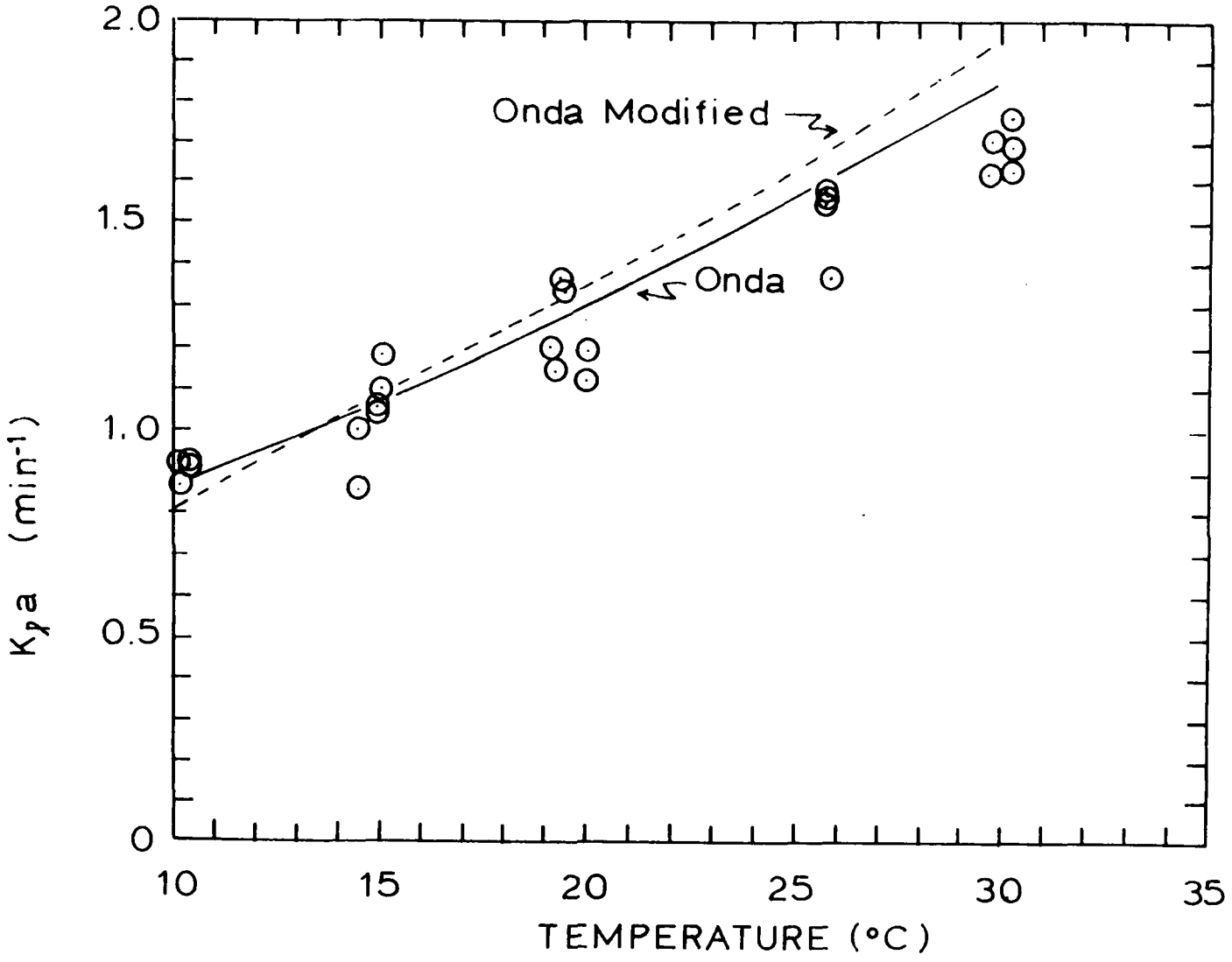

Figure 33. Estimated and Measured $K_\ell a$'s for Tetrachloroethylene. (1-Inch Polypropylene Pall Rings, L_v = 1.36 m·min^{-1}, G_v = 10.95 m·min^{-1} [Ref: 25°C, 1 atm]).

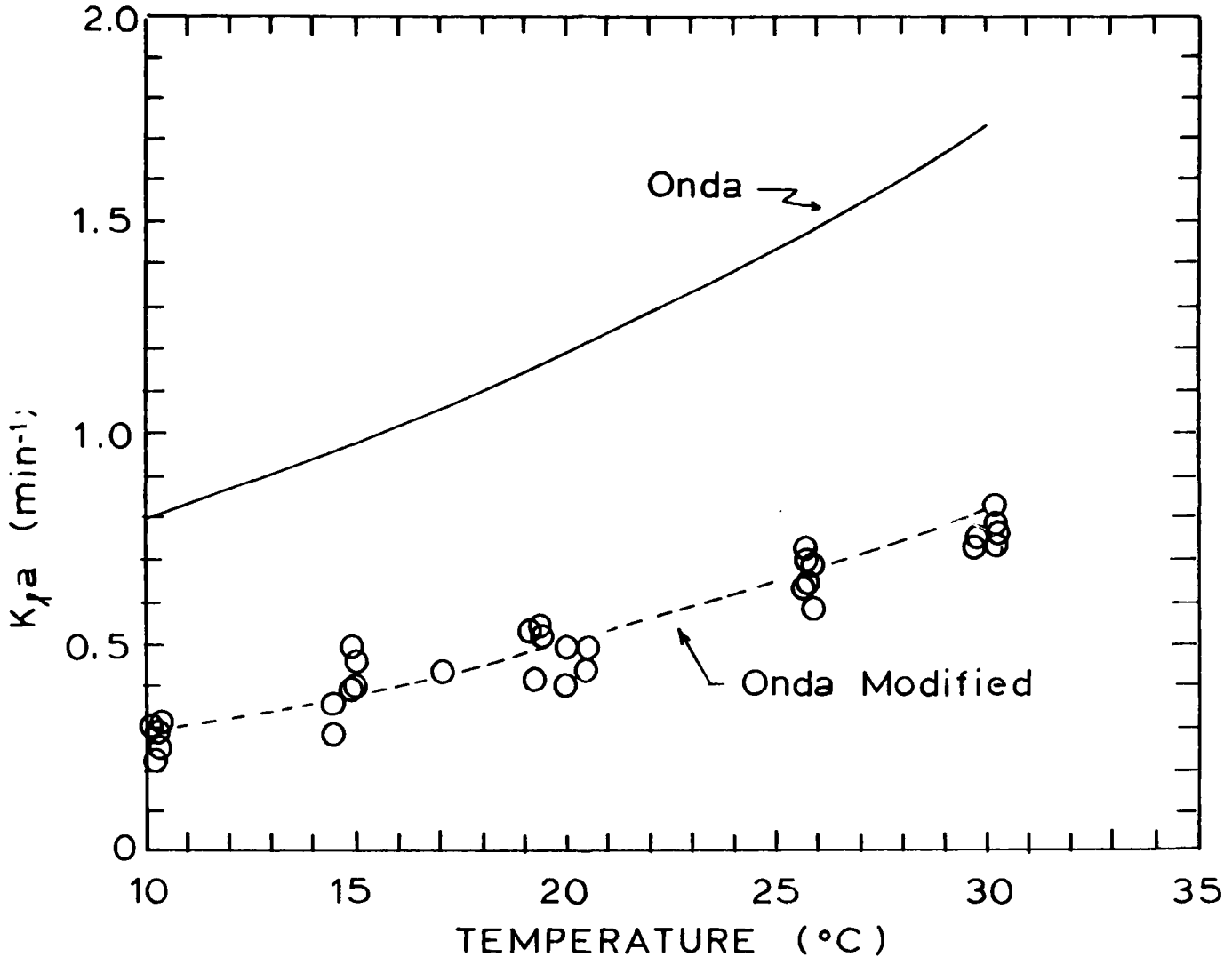

Figure 34. Estimated and Measured $K_\ell a$'s for Methylene Chloride. (1-Inch Polypropylene Pall Rings, L_v = 1.36 m·min^{-1}, G_v = 10.95 m·min^{-1} [Ref: 25°C, 1 atm]).

the front-constants in the Onda k_ℓ and k_g expressions. Thirdly, there is no reason to believe that the modification factors λ and ϕ should be applied solely to the k_ℓ and k_g correlations. Strictly speaking, λ and ϕ are modifying ($k_\ell a$) and ($k_g a H_c$) expressions. Thus, some of the "error" may be (and probably is) contained in the "a" expression, Equation (46). But from a practical standpoint, a constant factor error in "a" is irrelevant, being incorporated in both λ and ϕ, since k_ℓ and k_g are never employed without their being multipled by "a."

3. Effect of Packing Type, Size and Loading Rates on $K_\ell a$

a. Scope

Using seven different packings, $K_\ell a$ values were determined for each of the five study compounds over a range of liquid and gas loadings. All studies were conducted at 25°C and employed mixtures of all five compounds, predissolved in 500 ml methanol prior to addition to the reservoir. Approximate reservoir concentrations were those earlier shown in Table 39.

At least three replicate stripping runs were made at each of the operating conditions studied. This included six packings and six liquid loadings and four to seven gas loadings. (The seventh packing, 1 1/2-inch Pall rings, was not as extensively studied).

In studies of the effect of liquid flow variation, the gas loading was held constant and the liquid loading, L_v, was varied over six different values; 0.60, 0.78, 0.92, 1.10, 1.24 and 1.38 m/min. The maximum liquid loading was determined by the capacity of the drainage system. The constant gas loading differed among packings, based upon the maximum flow achievable at a liquid loading of 1.38 m/min. Gas loadings, G_v, were: 32.9 m/min for 5/8-inch Pall rings, 2-inch Tri-Packs, and Flexipac; 25.6 m/min for 1-inch Pall rings and 1-inch Flexisaddles; and 50.2 m/min for 2-inch Pall rings.

Gas flow variation was studied at a constant liquid loading of 0.92 m/min. Seven gas loadings were studied for 5/8-inch rings, ranging from 4.56 to 36.5 m/min. One-inch rings were tested at four loadings in the range of 4.56 to 41.1 m/min; 2-inch rings were tested at five loadings from 4.56 to 50.2 m/min; Flexisaddles were tested at five gas loadings ranging from 7.30 to 41.1 m/min; and

2-inch Tri-Packs and were tested at five loadings from 4.56 to 54.75 m/min.

$K_\ell a$ measurements for all conditions studied are presented in Tables 45 through 57. At least three runs were made under each condition studied. Coefficients of variation between replicate runs, [CV = (mean/standard deviation)*100], are generally less than 10 percent, though at low gas flow rates the variation for methylene chloride increases. Coefficients of determination, r^2, for the linear regression used to determine $K_\ell a$ (Equation 103) were greater than 0.99 for most cases. The main exception was found at low gas flows, where r^2 was lower.

b. Effect of Liquid Loading

As expected, $K_\ell a$'s for all five compounds increase as liquid loading increases, with the observed values of $K_\ell a$ showing little variation among the compounds for a given flow rate and packing. A sample plot is shown in Figure 35 for 2-inch Pall rings. The standard deviation among compounds is, on the average, only 9 percent, with the highest deviations occurring at high liquid loadings.

It is interesting to note that methylene chloride (the least volatile compound) has the highest $K_\ell a$ value at low liquid loadings, whereas tetrachloroethylene (the most volatile compound) has the lowest. A certain amount of repositioning then occurs in relative $K_\ell a$ values among the five compounds as L_v increases, caused by an increase in the relative importance of gas-phase resistance with increasing L_v at constant G_v. (Recall that the trend in relative D_ℓ values among the compounds was exactly opposite to the trend in relative H_c values. Changes in % R_g with changes in L_v and/or G_v can induce such difference in relative positioning of $K_\ell a$ values among the five compounds.) Thus, no generalizations are possible concerning the correlation of $K_\ell a$ with either D_ℓ or H_c .

c. Effect of Gas Loading

The observed values of $K_\ell a$ show different dependencies on gas flow among the solutes. As an example, Figure 36 shows $K_\ell a$

TABLE 45. $K_L a$ DATA -- 5/8-INCH PALL RINGS, CONSTANT G_v = 32.9 m·min^{-1}, T = 25°C.

L_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_L a}$ (min^{-1})	0.957	1.092	1.053	1.053	1.255
	CV (%)	6.4	1.6	0.95	5.9	0.83
	n	3	3	3	3	3
0.78	$\overline{K_L a}$ (min^{-1})	1.297	1.397	1.354	1.314	1.497
	CV (%)	6.6	2.9	8.2	5.5	2.6
	n	4	4	4	4	4
0.92	$\overline{K_L a}$ (min^{-1})	1.417	1.561	1.532	1.384	1.618
	CV (%)	9.4	1.0	3.6	6.4	6.6
	n	4	4	4	4	4
1.10	$\overline{K_L a}$ (min^{-1})	1.723	1.796	1.833	1.694	1.880
	CV (%)	7.1	3.2	5.6	5.6	3.7
	n	4	4	4	4	4
1.24	$\overline{K_L a}$ (min^{-1})	1.800	1.947	1.939	1.824	1.987
	CV (%)	7.5	3.6	3.7	4.3	3.8
	n	4	4	4	4	4
1.38	$\overline{K_L a}$ (min^{-1})	2.121	2.117	2.104	1.928	2.010
	CV (%)	5.2	3.3	4.9	6.6	3.8
	n	5	5	5	3	3

TABLE 46. $K_L a$ DATA -- 1-INCH PALL RINGS, CONSTANT G_v = 25.6 m·min^{-1}, T = 25°C.

L_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_L a}$ (min^{-1})	0.87	0.95	0.95	0.90	0.96
	CV (%)	7.7	4.5	4.1	3.1	1.5
	n	3	3	3	4	3
0.78	$\overline{K_L a}$ (min^{-1})	1.07	1.25	1.21	1.12	1.24
	CV (%)	3.8	4.0	3.9	3.1	7.9
	n	5	5	5	5	4
0.92	$\overline{K_L a}$ (min^{-1})	1.22	1.36	1.31	1.27	0.95
	CV (%)	8.4	4.0	3.7	10.8	5.3
	n	3	4	4	4	4
1.10	$\overline{K_L a}$ (min^{-1})	1.38	1.59	1.49	1.27	1.28
	CV (%)	6.9	2.6	4.2	2.4	4.5
	n	6	7	7	7	5
1.24	$\overline{K_L a}$ (min^{-1})	1.56	1.77	1.64	1.35	1.37
	CV (%)	1.9	3.8	4.1	3.2	5.1
	n	3	4	4	4	3
1.38	$\overline{K_L a}$ (min^{-1})	1.97	2.16	2.07	1.74	1.75
	CV (%)	2.1	3.0	3.5	4.6	3.4
	n	3	4	4	5	5

TABLE 47. $K_{\ell}a$ DATA -- 2-INCH PALL RINGS, CONSTANT G_v = 50.2 m·min^{-1}, T = 25°C.

L_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_{\ell}a}$ (min^{-1})	0.80	0.88	0.88	0.84	0.94
	CV (%)	5.1	0.5	0.8	2.3	2.9
	n	3	3	3	5	5
0.78	$\overline{K_{\ell}a}$ (min^{-1})	1.04	1.12	1.13	1.05	1.16
	CV (%)	5.6	4.7	4.1	3.8	4.1
	n	4	3	3	4	4
0.92	$\overline{K_{\ell}a}$ (min^{-1})	1.22	1.24	1.27	1.15	1.26
	CV (%)	1.0	2.1	1.7	4.4	4.7
	n	4	3	4	4	4
1.10	$\overline{K_{\ell}a}$ (min^{-1})	1.31	1.44	1.42	1.36	1.48
	CV (%)	2.5	0.5	1.3	0.3	0.3
	n	3	3	3	3	3
1.24	$\overline{K_{\ell}a}$ (min^{-1})	1.43	1.52	1.50	1.41	1.52
	CV (%)	3.1	4.8	3.9	3.5	3.5
	n	3	3	3	4	4
1.38	$\overline{K_{\ell}a}$ (min^{-1})	1.57	1.68	1.64	1.52	1.64
	CV (%)	3.0	1.1	0.9	1.1	2.6
	n	3	3	3	3	3

TABLE 48. $K_g a$ DATA -- 1-INCH FLEXISADDLES, CONSTANT G_v = 25.6 m·min^{-1}, T = 25°C.

L_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_g a}$ (min^{-1})	0.73	0.81	0.81	0.73	0.83
	CV (%)	4.7	7.2	8.1	4.6	3.8
	n	3	3	3	3	3
0.78	$\overline{K_g a}$ (min^{-1})	0.88	1.03	1.02	0.94	1.01
	CV (%)	5.4	2.6	3.8	6.7	2.6
	n	3	3	3	3	3
0.92	$\overline{K_g a}$ (min^{-1})	1.04	1.16	1.17	1.06	1.10
	CV (%)	5.3	6.8	3.7	7.3	5.0
	n	3	3	3	3	3
1.10	$\overline{K_g a}$ (min^{-1})	1.17	1.31	1.28	1.17	1.20
	CV (%)	8.0	2.5	1.1	0.2	3.4
	n	3	3	3	3	3
1.24	$\overline{K_g a}$ (min^{-1})	1.16	1.29	1.26	1.20	1.23
	CV (%)	11.3	13.8	12.8	6.9	6.9
	n	3	3	3	3	3
1.38	$\overline{K_g a}$ (min^{-1})	1.28	1.43	1.40	1.22	1.24
	CV (%)	2.8	3.2	3.3	1.7	5.1
	n	3	3	3	3	3

TABLE 49. $K_{\ell}a$ DATA -- 2-INCH TRI-PACKS, CONSTANT G_v = 32.9 m·min^{-1}, T = 25°C.

L_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_{\ell}a}$ (min^{-1})	0.936	1.04	1.03	0.966	1.07
	CV (%)	18.9	13.2	13.0	14.7	14.9
	n	3	3	3	3	3
0.78	$\overline{K_{\ell}a}$ (min^{-1})	1.11	1.18	1.16	1.11	1.18
	CV (%)	6.2	4.8	5.1	4.9	6.0
	n	3	3	3	3	3
0.92	$\overline{K_{\ell}a}$ (min^{-1})	1.35	1.37	1.36	1.31	1.37
	CV (%)	4.3	4.0	3.9	2.6	2.6
	n	3	3	3	3	3
1.10	$\overline{K_{\ell}a}$ (min^{-1})	1.44	1.51	1.47	1.38	1.47
	CV (%)	2.9	3.0	2.6	1.3	1.9
	n	3	3	3	3	3
1.24	$\overline{K_{\ell}a}$ (min^{-1})	1.71	1.77	1.74	1.65	1.76
	CV (%)	1.6	1.8	2.6	3.9	4.7
	n	3	3	3	3	3
1.38	$\overline{K_{\ell}a}$ (min^{-1})	1.86	1.89	1.87	1.76	1.87
	CV (%)	6.1	6.7	5.4	4.1	3.3
	n	3	3	3	3	3

TABLE 50. $K_L a$ DATA -- FLEXIPAC, CONSTANT G_v = 32.9 m•min^{-1}, T = 25°C.

L_v (m•min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
0.60	$\overline{K_L a}$ (min^{-1})	0.601	0.607	0.625	0.535	0.607
	CV (%)	3.0	0.01	3.2	8.8	1.7
	n	3	3	3	3	3
0.78	$\overline{K_L a}$ (min^{-1})	0.755	0.766	0.759	0.705	0.750
	CV (%)	2.2	2.0	3.0	2.2	1.5
	n	3	3	3	3	3
0.92	$\overline{K_L a}$ (min^{-1})	0.866	0.893	0.865	0.771	0.795
	CV (%)	6.8	4.8	6.0	7.2	9.8
	n	3	3	3	3	3
1.10	$\overline{K_L a}$ (min^{-1})	1.02	1.07	1.02	0.874	0.846
	CV (%)	3.4	0.74	1.6	4.0	6.4
	n	3	3	3	3	3
1.24	$\overline{K_L a}$ (min^{-1})	1.21	1.23	1.18	0.991	0.947
	CV (%)	1.9	1.7	2.1	3.4	2.0
	n	3	3	3	3	3
1.38	$\overline{K_L a}$ (min^{-1})	1.18	1.29	1.18	0.993	0.879
	CV (%)	3.3	1.2	2.0	4.1	7.2
	n	3	3	3	3	3

TABLE 51. $K_{\ell}a$ DATA -- 5/8-INCH PALL RINGS, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
4.56	$\overline{K_{\ell}a}$ (min^{-1})	1.33	1.36	1.28	1.29	1.68
	CV (%)	4.1	1.1	6.1	----	----
	n	4	3	4	1	1
7.3	$\overline{K_{\ell}a}$ (min^{-1})	1.43	1.47	1.35	1.09	1.01
	CV (%)	5.9	5.6	5.3	9.2	17.5
	n	4	4	4	4	4
11.0	$\overline{K_{\ell}a}$ (min^{-1})	1.47	1.54	1.47	1.27	1.29
	CV (%)	5.2	4.3	2.9	3.0	15.5
	n	4	4	3	2	2
16.4	$\overline{K_{\ell}a}$ (min^{-1})	1.49	1.62	1.58	1.44	1.43
	CV (%)	5.0	1.9	2.6	6.4	4.4
	n	4	4	4	4	3
25.6	$\overline{K_{\ell}a}$ (min^{-1})	1.41	1.58	1.49	1.40	1.53
	CV (%)	6.8	1.4	8.3	3.9	3.4
	n	4	4	4	3	3
32.9	$\overline{K_{\ell}a}$ (min^{-1})	1.42	1.56	1.53	1.39	1.62
	CV (%)	9.4	1.0	3.6	6.4	6.6
	n	4	4	4	4	4
36.5	$\overline{K_{\ell}a}$ (min^{-1})	1.52	1.60	1.61	1.51	1.73
	CV (%)	4.2	1.6	2.6	7.4	4.7
	n	3	3	3	3	3

TABLE 52. $K_g a$ DATA -- 1-INCH PALL RINGS, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
4.56	$\overline{K_g a}$ (min^{-1})	1.08	1.14	0.84	0.29	0.10
	CV (%)	4.8	2.7	4.3	12.4	10.9
	n	5	5	5	3	4
16.3	$\overline{K_g a}$ (min^{-1})	1.25	1.38	1.29	1.08	1.01
	CV (%)	5.9	1.8	2.9	4.2	1.1
	n	3	3	3	3	3
25.6	$\overline{K_g a}$ (min^{-1})	1.21	1.37	1.32	1.21	1.19
	CV (%)	7.6	4.2	4.0	4.0	2.8
	n	4	5	5	6	5
41.1	$\overline{K_g a}$ (min^{-1})	1.35	1.54	1.46	1.34	1.48
	CV (%)	4.7	4.3	3.0	6.9	6.7
	n	4	4	4	3	3

TABLE 53. $K_\ell a$ DATA -- 2-INCH PALL RINGS, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
4.56	$\overline{K_\ell a}$ (min^{-1})	1.00	1.04	0.88	0.61	0.40
	CV (%)	9.0	6.8	8.6	----	----
	n	4	4	2	1	1
7.30	$\overline{K_\ell a}$ (min^{-1})	1.12	1.16	1.05	0.78	0.59
	CV (%)	3.2	3.4	4.3	9.4	----
	n	4	3	4	3	1
14.6	$\overline{K_\ell a}$ (min^{-1})	1.17	1.21	1.17	1.00	0.97
	CV (%)	4.2	3.9	3.0	1.8	2.8
	n	3	3	3	3	3
27.4	$\overline{K_\ell a}$ (min^{-1})	1.15	1.23	1.23	1.09	1.14
	CV (%)	4.3	1.1	1.7	7.1	4.2
	n	3	3	3	3	3
50.2	$\overline{K_\ell a}$ (min^{-1})	1.22	1.24	1.27	1.15	1.26
	CV (%)	1.0	2.1	1.7	4.4	4.9
	n	4	3	4	4	4

TABLE 54. $K_L a$ DATA -- 1-INCH FLEXISADDLES, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
7.30	$\overline{K_L a}$ (min^{-1})	0.91	0.98	0.89	0.63	0.44
	CV (%)	8.8	4.2	6.4	2.8	9.3
	n	3	3	3	3	3
14.6	$\overline{K_L a}$ (min^{-1})	0.97	1.04	1.00	0.85	0.80
	CV (%)	8.8	8.9	0.5	0.6	4.8
	n	3	3	3	3	3
18.3	$\overline{K_L a}$ (min^{-1})	1.08	1.17	1.15	0.95	0.94
	CV (%)	4.4	7.6	0.4	1.7	0.2
	n	3	3	3	3	3
25.6	$\overline{K_L a}$ (min^{-1})	1.04	1.16	1.17	1.06	1.10
	CV (%)	5.3	6.8	3.7	7.3	5.0
	n	3	3	3	3	3
41.1	$\overline{K_L a}$ (min^{-1})	1.15	1.33	1.34	1.17	1.19
	CV (%)	13.0	1.7	3.9	4.9	1.3
	n	3	3	3	3	3

TABLE 55. $K_\ell a$ DATA -- 2-INCH TRI-PACKS, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
4.56	$\overline{K_\ell a}$ (min^{-1})	1.27	1.30	1.20	1.07	0.882
	CV (%)	4.7	4.1	2.9	7.4	4.8
	n	3	3	3	3	2
7.30	$\overline{K_\ell a}$ (min^{-1})	1.29	1.32	1.25	1.14	0.972
	CV (%)	1.6	1.1	4.4	17.3	10.2
	n	3	3	3	3	3
14.6	$\overline{K_\ell a}$ (min^{-1})	1.36	1.37	1.34	1.23	1.27
	CV (%)	2.0	1.6	0.9	4.9	2.0
	n	3	3	3	3	3
32.8	$\overline{K_\ell a}$ (min^{-1})	1.35	1.37	1.36	1.31	1.37
	CV (%)	4.3	4.0	3.9	2.6	2.6
	n	3	3	3	3	3
54.8	$\overline{K_\ell a}$ (min^{-1})	1.35	1.39	1.37	1.28	1.46
	CV (%)	5.4	4.7	4.8	8.7	6.2
	n	3	3	3	3	3

TABLE 56. $K_g a$ DATA -- FLEXIPAC, CONSTANT L_v = 0.92 m·min^{-1}, T = 25°C.

G_v (m·min^{-1})		Tetrachloroethylene	1,1,1-Trichloroethane	Trichloroethylene	Chloroform	Methylene Chloride
4.56	$\overline{K_g a}$ (min^{-1})	0.701	0.736	0.615	0.317	0.173
	CV (%)	11.9	8.3	6.6	7.2	5.7
	n	3	3	3	2	2
7.30	$\overline{K_g a}$ (min^{-1})	0.830	0.889	0.795	0.514	0.347
	CV (%)	13.8	6.5	8.8	4.6	1.8
	n	3	3	3	2	2
14.6	$\overline{K_g a}$ (min^{-1})	0.896	0.939	0.883	0.750	0.687
	CV (%)	4.1	1.7	3.8	3.7	7.3
	n	3	3	3	3	3
32.8	$\overline{K_g a}$ (min^{-1})	0.866	0.893	0.865	0.771	0.795
	CV (%)	6.8	4.8	6.0	7.2	9.8
	n	3	3	3	3	3
54.8	$\overline{K_g a}$ (min^{-1})	0.956	0.990	0.995	0.955	1.03
	CV (%)	7.5	2.2	3.8	1.6	4.1
	n	3	3	3	3	3

TABLE 57. $K_{\ell}a$ DATA -- 1-1/2-INCH PALL RINGS, T = 25°C.

L_v ($m \cdot min^{-1}$)	G_v ($m \cdot min^{-1}$)		Tetrachloro-ethylene	1,1,1-Trichloro-ethane	Trichloro-ethylene	Chloroform	Methylene Chloride
0.60	25.6	$\overline{K_{\ell}a}$ (min^{-1})[a]	0.668	0.724	0.705	0.653	0.661
		% Δ[b]	0.3	7.1	5.1	7.0	12.0
		$(K_{\ell}a)_U$ (min^{-1})[c]	0.754	0.776	0.779	0.770	0.793
		% D[d]	12.9	7.2	10.5	17.9	20.0
	32.3	$\overline{K_{\ell}a}$ (min^{-1})	0.667	0.745	0.703	0.704	0.734
		% Δ	3.2	6.6	0.1	2.7	11.0
		$(K_{\ell}a)_U$ (min^{-1})	0.757	0.779	0.784	0.782	0.810
		% D	13.5	4.6	11.5	11.1	10.4
	50.2	$\overline{K_{\ell}a}$ (min^{-1})	0.760	0.836	0.833	0.808	0.869
		% Δ	2.1	8.6	8.7	7.3	9.2
		$(K_{\ell}a)_U$ (min^{-1})	0.761	0.784	0.792	0.800	0.837
		% D	0.1	-6.2	-4.9	-1.0	-3.7

TABLE 57. $K_\ell a$ DATA -- 1-1/2-INCH PALL RINGS, T = 25°C (CONCLUDED).

L_v (m·min^{-1})	G_v (m·min^{-1})		Tetrachloro-ethylene	1,1,1-Trichloro-ethane	Trichloro-ethylene	Chloroform	Methylene Chloride
1.24	25.6	$\overline{K_\ell a}$ (min^{-1})	1.19	1.36	1.31	1.21	1.17
		% Δ	4.9	4.2	5.9	3.1	1.9
		$(K_\ell a)_o$ (min^{-1})	1.29	1.33	1.33	1.28	1.30
		% D	8.4	-2.2	1.5	5.8	11.1
	32.3	$K_\ell a$ (min^{-1})	1.17	1.32	1.26	1.16	1.23
		% Δ	1.2	1.5	1.8	0.68	1.6
		$(K_\ell a)_o$ (min^{-1})	1.30	1.34	1.34	1.31	1.34
		% D	11.1	1.5	6.3	12.9	8.9

[a] Mean of two replicate runs.

[b] % difference between the two replicate values.

[c] Based upon Onda correlations.

[d] $[(K_\ell a)_o - (K_\ell a)_m]\ 100/(K_\ell a)_m$.

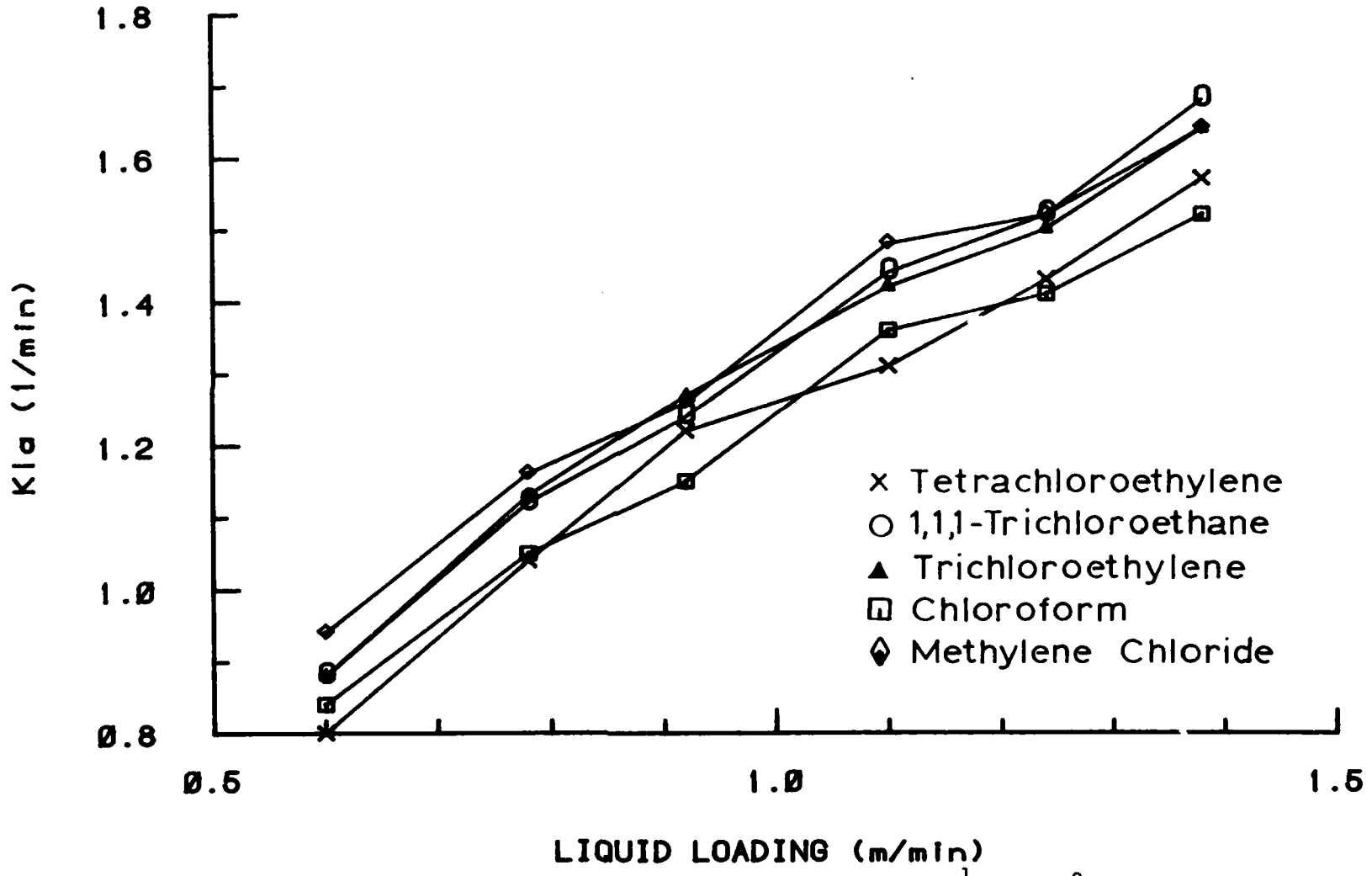

Figure 35. $K_\ell a$ Versus Liquid Loading (2-Inch Pall Rings; G_V = 50.2 m·min^{-1}; T = 25°C).

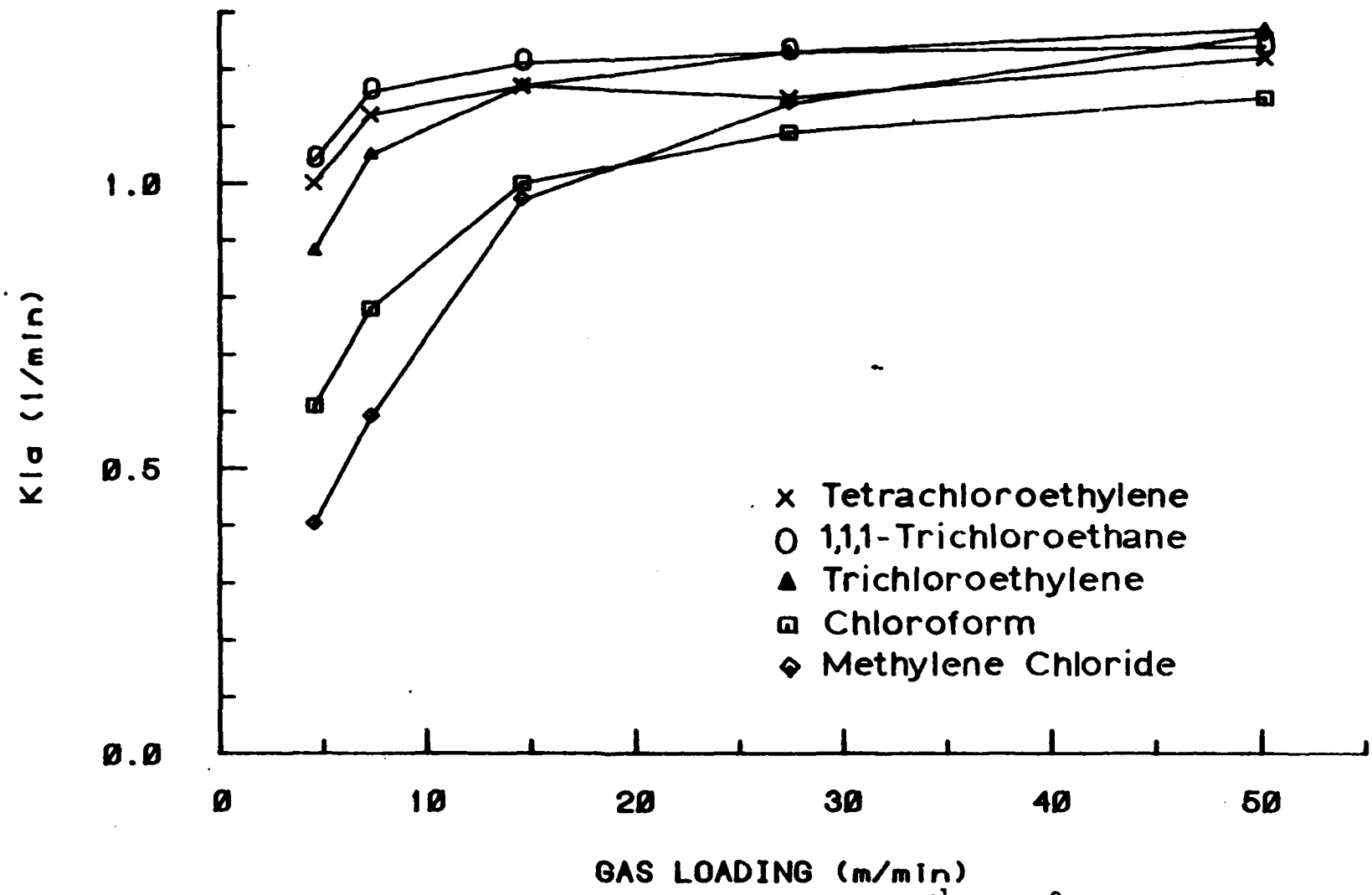

Figure 36. $K_\ell a$ Versus Gas Loading (2-Inch Pall Rings; L_V = 0.92 m·min^{-1}, T = 25°C).

versus gas loading (at constant L_v) for each compound measured when the tower was packed with 2-inch Pall rings. This graph shows $K_\ell a$ to be nearly independent of gas flow for the most volatile compounds, tetrachloroethylene, 1,1,1-trichloroethane, and trichloroethylene, except at the lowest loading where $K_\ell a$ drops. In contrast, the less volatile methylene chloride and chloroform show greater dependence of $K_\ell a$ on gas loading. These findings are consistent with the two-resistance model, which predicts increased % R_g as H_c decreases (for a given packing, L_v and G_v). Systems with higher % R_g are more affected by increasing G_v than are systems with neglible % R_g.

d. Effect of Packing

Sample plots of data comparing the six packings extensively studied are contained in Figures 37 and 38. The first shows the effect of liquid loading upon the $K_\ell a$ of TCE for each of six different packings. Unfortunately, the use of different G_v values among the packings prohibits direct comparison of the different packings' $K_\ell a$ values. All that can be said is that the trend of $K_\ell a$ with L_v is similar among the packings. It also appears that $K_\ell a$ decreases as packing size increases, in accordance with accepted theory.

Figure 38 shows the effect of gas loading on the $K_\ell a$ of TCE for the different packings, all at constant L_v. It appears that among Pall rings, $K_\ell a$ decreases with increasing size. The general slope trends also suggest that both 1-inch Pall rings and 1-inch Flexisaddles exhibit greater % R_g than the other packings (for unknown reasons).

Examination of the TCE data shows that $K_\ell a$ values for 2-inch Tri-Packs were, on average 14 percent higher (range: 3 to 36 percent) than $K_\ell a$ values for 2-inch Pall rings under comparable loading conditions. Similar findings are obtained by comparison of data from the other compounds. Likewise, $K_\ell a$ values for 1-inch Pall rings were, on average, 20 percent higher (range: 9 to 48 percent) than comparable $K_\ell a$ values for 1-inch Flexisaddles. However, it must be emphasized that $K_\ell a$ is only one of several considerations that should influence packing selection; packing capital cost and head-loss considerations

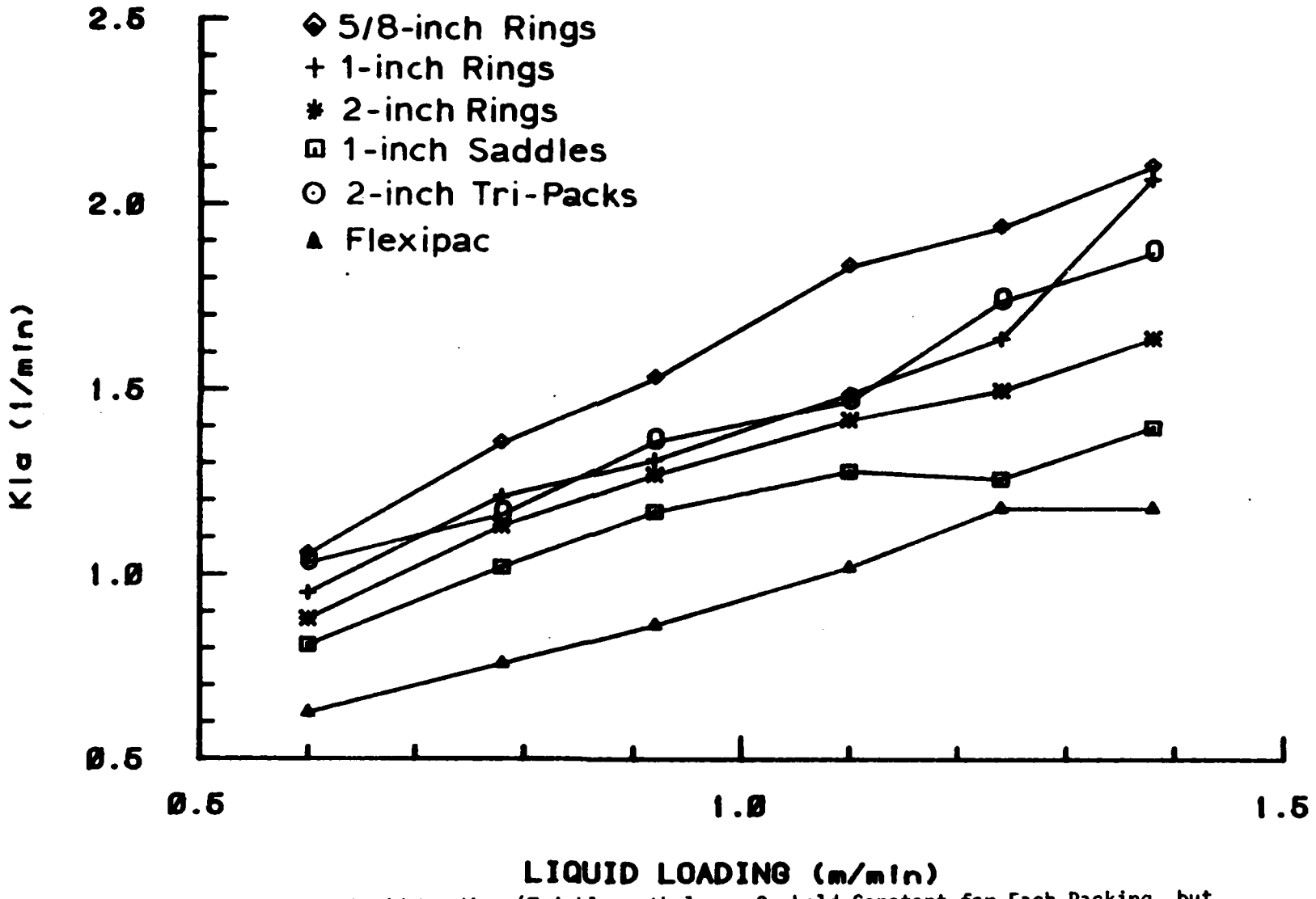

Figure 37. $K_\ell a$ Versus Liquid Loading (Trichloroethylene; G_v held Constant for Each Packing, but Varied Among Packings, T = 25°C).

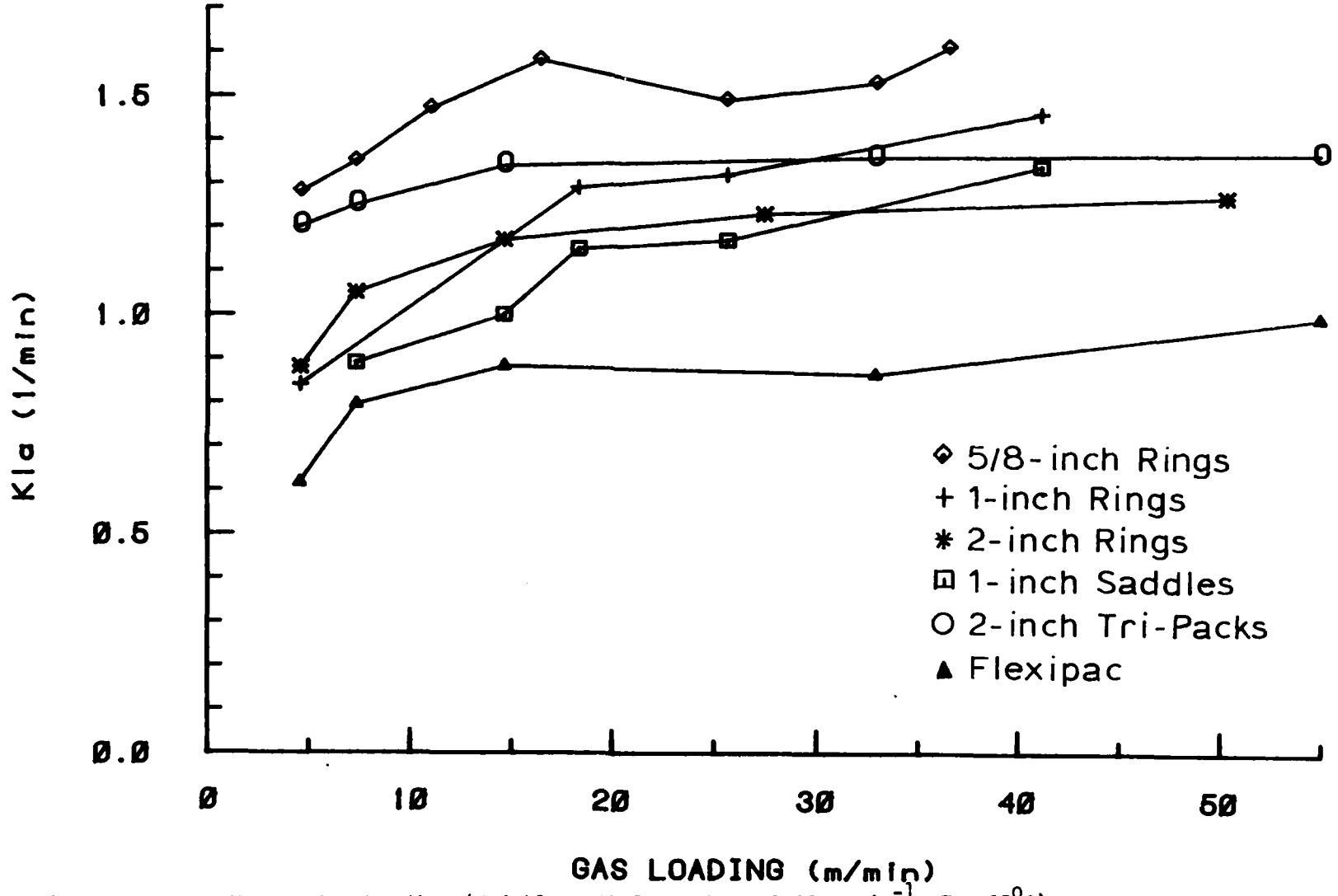

Figure 38. $K_\ell a$ Versus Gas Loading (Trichloroethylene; L_V = 0.92 m·min^{-1}, T = 25°C).

are also very important. Overall capital plus operation/maintenance costs should dictate packing selection; these will vary among specific installations.

Comparison of mass transfer coefficients for different packings is more an indication of differences in effective interfacial area than of any other single parameter. The difference in $K_\ell a$'s for 1-inch Pall rings and 1-inch Flexisaddles is a good example. These two packings have the same dry surface area per unit packed volume, and the same nominal diameter (d_p = 0.0254 m). They were tested under the same gas and liquid flow rates, yet, $K_\ell a$'s measured with 1-inch rings averaged 20 percent higher than $K_\ell a$'s measured for 1-inch Flexisaddles.

Liquid flow patterns over the two packing types were visually quite different. Water flowing over the saddles appeared to cascade in thin sheets from one piece of packing to the next. Flow over the rings seemed to be less cohesive. Water appeared to form small drops which fell from one piece of packing, and broke into smaller drops upon hitting the next piece of packing. This formation and reformation of drops would seem to renew the effective area for transfer much more efficiently than the sheeting action observed with saddles. Wall channeling also seemed more evident when saddles were used, which also would reduce effective interfacial area, and thus $K_\ell a$.

It is apparent that the Flexipac structured packing yielded considerably lower $K_\ell a$ values than any of the other packings. However, the fit of this packing to our column was improper. Though the ID dimensions of the column varied only within the range from 44.475 to 44.514 cm -- and these dimensions were suppied to the manufacturer -- the packing was found to be roughly elliptical in cross-section, 41.9 by 44.4 cm (with wiper cords in place). Additionally, no installation instructions were provided. As a result, the individual 30.5 cm high elements were randomly arranged, rather than placing them so that each successive element was rotated 90° with respect to the element below it. This deficiency, however, is judged to be of far lesser significance than the approximately 2.5 cm gap

between some portions of some elements and the column inner wall. Wall-channeling of the liquid was obvious, and similar channeling of the gas may be presumed. As a result, the data obtained with this Flexipac is probably not representative of the potential capabilities of this packing.

4. Pressure Drop

Pressure drop through a packed column is a major determinant in the economics of tower operation. A pressure drop of 8 cm per meter of packing (1 in/ft) is usually suggested as the upper limit of economical operation.

The pilot facility was equipped with a water-filled manometer to measure pressure differentials across the length of the column. The manometer was connected to the air ducts at the entrance and exit from the tower. Pressure differentials were recorded at the beginning and end of each stripping run. In Table 58, measured pressure drops are compared with pressure drops predicted by Eckert's generalized correlation (Figure 18-39 in Perry and Chilton, 1973) and with data supplied by the packing manufacturers.

As Table 58 indicates, the correlations are not consistently accurate at predicting pressure drops across the column. In some cases predicted and measured values are essentially equal, while, in other cases, the values are not even close. There does not appear to be any trend in the deviations, and there is no immediately apparent reason for the difference between measured and predicted values.

The lack of agreement often evident between our measurements of pressure drop and estimations provided through use of the various correlations prompted concern over our technique. To determine whether the points of measurement were appropriate, they were changed. Pressure differentials, which were normally measured between air ducts at the top and the bottom of the column, were compared with differentials measured directly across the packed portion of the column (between Ports 8 and 0). For this comparison, various liquid and gas flows were employed with 1-inch Pall rings. Differentials measured using both procedures were equal for all conditions tested, implying negligible inlet and outlet losses. Pressure differentials

TABLE 58. PRESSURE DROP (inches of H_2O per foot of packing).

L_m	5/8-inch Pall Rings				1-inch Pall Rings				2-inch Pall Rings			
$(lb \cdot hr^{-1} \cdot ft^{-2})$	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.[a]	Mfg.[b]	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.
7,300	480	0.21	0.21	0.20	370	0.11	0.08	NA	730	0.14	0.08	NA
11,000	66	0.01	NA[c]	NA	66	0.01	NA	NA	66	0.006	NA	NA
11,000	480	0.30	0.38	0.33	370	0.14	0.10	NA	400	0.02	0.05	NA
11,000	530	0.42	0.31	0.50	540	0.50	0.21	0.15	730	0.16	0.12	0.14
17,000	480	0.60	0.47	1.2	370	0.69	0.25	0.12	730	0.26	0.21	0.17

L_m	Flexipac				1-inch Flexisaddles				2-inch Tri-Packs			
$(lb \cdot hr^{-1} \cdot ft^{-2})$	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.
7,300	480	0.05	0.05	NA	370	0.06	0.08	NA	480	0.04	<0.05	<0.02
11,000	66	0.01	NA	NA	66	0.005	NA	NA	66	0.01	NA	NA
11,000	480	0.06	0.07	NA	370	0.08	0.10	2.0	480	0.04	<0.05	0.02
11,000	800	0.17	0.57	NA	540	0.26	0.21	NA	800	0.15	0.08	0.08
17,000	480	0.16	0.07	NA	370	0.11	0.25	NA	480	0.06	0.05	0.04

L_m	1 1/2-inch Pall Rings			
$(lb \cdot hr^{-1} \cdot ft^{-2})$	G_m $(lb \cdot hr^{-1} \cdot ft^{-2})$	Meas.	Gen.	Mfg.
7,300	370	0.05	0.07	NA
7,300	480	0.07	0.08	NA
7,300	730	0.17	0.15	0.15
15,000	370	0.07	0.09	NA
15,000	490	0.13	0.45	0.13

Notes

[a] Eckert's generalized pressure drop curves (Figure 18-39 in Perry and Chilton, 1973).

[b] From manufacturer's curves.

[c] NA indicates operating conditions were beyond range given in curves.

were also measured through the column without packing, to determine if there were significant losses due to the packing support plate. Manometer readings were taken with and without the support plate in place at several different gas loadings, with no liquid flowing and at a few different liquid loadings. The pressure drop aross the column was the same with or without the support plate, when there was no liquid flowing, and at a liquid loading of 1.4 m/min.

The results of these tests give no indication of why predicted and measured pressure drops do not agree. It is possible that the correlations simply do not scale down well to a column of the size used here. In general, caution should be used when applying any of the estimation methods for design purposes, especially at high liquid flows.

5. Evaluation of Onda Correlations

For all of the conditions studied, $K_\ell a$ values were calculated using the Onda correlations, Equations (44), (45), and (46), in conjunction with the two-resistance model, Equation (31). (Input parameter values were detailed in Table 33). These estimates of $K_\ell a$ are compared with observed values in Tables 59 and 60. Also appearing in the tables are the percentages of gas-phase resistance (% R_g) as predicted by the Onda correlations. (Note: data on 1 1/2-inch Pall rings were previously presented in Table 57).

Sample plots showing the effects of liquid loading on predicted and observed $K_\ell a$ values are shown in Figures 39 and 40. The "X"'s are data from Table 59; the curves are predictions made using the Onda correlations. Similar sample plots are shown in Figures 41 through 44 for the effect of gas loading on predicted and observed $K_\ell a$ values. All other packings and compounds showed trends similar to these sample plots: reasonably good agreement between Onda-predicted and observed $K_\ell a$ values; insensitivity of $K_\ell a$ to G_v for highly volatile compounds such as tetrachloroethylene (except at extremely low G_v values); and apparent underestimation by Onda of gas-phase resistance, as evidenced by plots of $K_\ell a$ vs G_v for low-volatility compounds such as methylene chloride (Figures 42 and 44). Underestimation of gas-phase resistance would only be noticed in cases of

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING)

5/8-Inch Pall Rings (G_v = 32.9 m·min^{-1})					1-Inch Pall Rings (G_v = 25.6 m·min^{-1})				
L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
	TETRACHLOROETHYLENE					TETRACHLOROETHYLENE			
0.60	1.01	0.96	5.2	1.3	0.60	0.88	0.87	1.1	2.1
0.78	1.24	1.30	-4.6	1.5	0.78	1.07	1.07	0.0	2.4
0.92	1.41	1.42	-0.7	1.6	0.92	1.22	0.21	0.8	2.6
1.10	1.61	1.72	-6.4	1.8	1.10	1.39	1.38	0.7	2.8
1.24	1.76	1.80	-2.2	1.9	1.24	1.52	1.56	-2.6	3.0
1.38	1.91	2.12	-9.9	2.0	1.38	1.64	1.97	-16.8	3.1
	1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE			
0.60	1.04	1.09	-4.6	1.4	0.60	0.91	0.95	-4.2	2.1
0.78	1.28	1.40	-8.6	1.5	0.78	1.10	1.25	-12.0	2.4
0.92	1.45	1.56	-7.1	1.6	0.92	1.25	1.36	-8.1	2.6
1.10	1.66	1.80	-7.8	1.8	1.10	1.43	1.59	-10.1	2.8
1.24	1.81	1.95	-7.2	1.9	1.24	1.56	1.77	-11.9	3.0
1.38	1.97	2.12	-7.1	2.0	1.38	1.69	2.16	-21.8	3.1

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING) (CONTINUED)

5/8-Inch Pall Rings (G_v = 32.9 m·min^{-1})					1-Inch Pall Rings (G_v = 25.6 m·min^{-1})				
L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
0.60	1.06	1.05	1.0	2.2	0.60	0.91	0.95	-4.2	3.5
0.78	1.29	1.35	-4.4	2.5	0.78	1.11	1.21	-8.3	4.0
0.92	1.46	1.53	-4.6	2.7	0.92	1.26	1.31	-3.8	4.3
1.10	1.67	1.83	-8.7	2.9	1.10	1.43	1.49	-4.0	4.6
1.24	1.83	1.94	-5.7	3.1	1.24	1.57	1.64	-4.3	4.9
1.38	1.98	2.10	-5.7	3.3	1.38	1.69	2.07	-18.4	5.1
CHLOROFORM					CHLOROFORM				
0.60	1.08	1.05	2.9	5.2	0.60	0.91	0.90	1.1	8.1
0.78	1.31	1.31	0.0	5.9	0.78	1.10	1.12	-1.8	9.1
0.92	1.48	1.38	7.2	6.3	0.92	1.24	1.27	-2.4	9.7
1.10	1.69	1.69	0.0	6.8	1.10	1.41	1.27	11.0	10.5
1.24	1.84	1.82	1.1	7.2	1.24	1.54	1.35	14.1	11.1
1.38	1.99	1.93	3.1	7.5	1.38	1.66	1.74	-4.6	11.6

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING) (CONTINUED)

L_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
5/8-Inch Pall Rings (G_v = 32.9 $m \cdot min^{-1}$)				
METHYLENE CHLORIDE				
0.60	1.13	1.25	-9.6	7.4
0.78	1.37	1.50	-8.7	8.2
0.92	1.55	1.62	-4.3	8.8
1.10	1.76	1.88	-6.4	9.5
1.24	1.92	1.99	-3.5	10.0
1.38	2.07	2.01	3.0	10.5
2-Inch Pall Rings (G_v = 50.2 $m \cdot min^{-1}$)				
TETRACHLOROETHYLENE				
0.60	0.73	0.80	-8.8	2.3
0.78	0.89	1.04	-14.4	2.6
0.92	1.01	1.22	-17.2	2.8
1.10	1.15	1.30	-11.5	3.1
1.24	1.25	1.43	-12.6	3.3
1.38	1.35	1.57	-14.0	3.4

L_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
1-Inch Pall Rings (G_v = 25.6 $m \cdot min^{-1}$)				
METHYLENE CHLORIDE				
0.60	0.95	0.96	-1.0	11.3
0.78	1.14	1.24	-8.1	12.6
0.92	1.28	1.20	6.7	13.5
1.10	1.45	1.28	13.3	14.5
1.24	1.58	1.37	15.3	15.2
1.38	1.70	1.75	-2.9	15.9
1-Inch Flexisaddles (G_v = 25.6 $m \cdot min^{-1}$)				
TETRACHLOROETHYLENE				
0.60	0.88	0.73	20.5	2.1
0.78	1.07	0.88	21.6	2.4
0.92	1.22	1.04	17.3	2.6
1.10	1.39	1.17	18.8	2.8
1.24	1.52	1.12	35.7	3.0
1.38	1.64	1.28	28.1	3.1

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING) (CONTINUED)

2-Inch Pall Rings (G_v = 50.2 m•min^{-1})					1-Inch Flexisaddles (G_v = 25.6 m•min^{-1})				
L_v (m•min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	L_v (m•min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE				
0.60	0.75	0.88	-14.8	2.3	0.60	0.91	0.81	12.3	2.1
0.78	0.92	1.12	-17.9	2.6	0.78	1.10	1.03	6.8	2.4
0.92	1.03	1.24	-16.9	2.8	0.92	1.25	1.16	7.8	2.6
1.10	1.18	1.44	-18.1	3.1	1.10	1.43	1.31	9.2	2.8
1.24	1.29	1.52	-15.1	3.3	1.24	1.56	1.29	20.9	3.0
1.38	1.39	1.68	-17.3	3.5	1.38	1.69	1.43	18.2	3.1
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
0.60	0.76	0.88	-13.6	3.8	0.60	0.91	0.81	12.3	3.5
0.78	0.92	1.13	-18.6	4.3	0.78	1.11	1.02	8.8	4.0
0.92	1.04	1.27	-18.1	4.7	0.92	1.26	1.17	7.7	4.3
1.10	1.18	1.41	-16.3	5.1	1.10	1.43	1.28	11.7	4.6
1.24	1.29	1.50	-14.0	5.4	1.24	1.57	1.26	24.6	4.9
1.38	1.39	1.64	-15.2	5.6	1.38	1.69	1.40	20.7	5.1

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_\ell a$ (CONSTANT GAS LOADING) (CONTINUED)

2-Inch Pall Rings (G_v = 50.2 m·min^{-1})					1-Inch Flexisaddles (G_v = 25.6 m·min^{-1})				
L_v (m·min^{-1})	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g	L_v (m·min^{-1})	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g
CHLOROFORM					CHLOROFORM				
0.60	0.75	0.84	-10.7	8.7	0.60	0.91	0.73	24.7	8.1
0.78	0.91	1.04	-12.5	9.8	0.78	1.10	0.94	17.0	9.1
0.92	1.02	1.15	-11.3	10.5	0.92	1.24	1.06	17.0	9.7
1.10	1.16	1.36	-14.7	11.4	1.10	1.41	1.16	21.6	10.5
1.24	1.26	1.41	-10.6	12.0	1.24	1.54	1.27	21.3	11.1
1.38	1.35	1.52	-11.2	12.6	1.38	1.66	1.22	36.1	11.6
METHYLENE CHLORIDE					METHYLENE CHLORIDE				
0.60	0.78	0.94	-17.0	12.1	0.60	0.95	0.83	14.5	11.3
0.78	0.94	1.16	-19.0	13.6	0.78	1.14	1.01	12.9	12.6
0.92	1.05	1.26	-16.7	14.5	0.92	1.28	1.10	16.4	13.5
1.10	1.19	1.48	-19.6	15.7	1.10	1.45	1.20	20.8	14.5
1.24	1.28	1.52	-15.8	16.5	1.24	1.58	1.17	35.0	15.2
1.38	1.38	1.64	-15.9	17.2	1.38	1.70	1.24	37.1	15.9

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING) (CONTINUED)

2-Inch Tri-Packs (G_v = 32.9 m•min^{-1})					Flexipac (G_v = 32.9 m•min^{-1})				
L_v (m•min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	L_v (m•min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
TETRACHLOROETHYLENE					TETRACHLOROETHYLENE				
0.60	0.87	0.94	-7.4	4.9	0.60	0.94	0.60	56.7	1.8
0.78	1.05	1.11	-5.4	5.5	0.78	1.14	0.76	50.0	2.0
0.92	1.18	1.35	-12.6	5.9	0.92	1.29	0.87	48.3	2.1
1.10	1.35	1.44	-6.3	6.4	1.10	1.48	1.02	45.1	2.3
1.24	1.47	1.71	-14.0	6.8	1.24	1.62	1.21	33.9	2.5
1.38	1.59	1.86	-14.5	7.2	1.38	1.76	1.18	49.2	2.6
1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE				
0.60	0.89	1.04	-14.4	4.9	0.60	0.96	0.61	57.4	1.8
0.78	1.08	1.18	-8.5	5.5	0.78	1.18	0.77	53.2	2.0
0.92	1.22	1.37	-10.9	6.0	0.92	1.33	0.89	49.4	2.2
1.10	1.39	1.51	-7.9	6.5	1.10	1.52	1.07	42.1	2.4
1.24	1.51	1.77	-14.7	6.9	1.24	1.67	1.23	35.8	2.5
1.38	1.64	1.89	-13.2	7.2	1.38	1.81	1.29	40.3	2.6

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT GAS LOADING) (CONTINUED)

2-Inch Tri-Packs (G_v = 32.9 m·min^{-1})					Flexipac (G_v = 32.9 m·min^{-1})				
L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	L_v (m·min^{-1})	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
0.60	0.88	1.03	-14.6	8.0	0.60	0.97	0.63	54.0	2.9
0.78	1.07	1.17	-8.5	8.9	0.78	1.19	0.76	56.6	3.3
0.92	1.20	1.36	-11.8	9.6	0.92	1.34	0.87	54.0	3.6
1.10	1.36	1.47	-7.5	10.4	1.10	1.53	1.02	50.0	3.9
1.24	1.48	1.74	-14.9	11.0	1.24	1.68	1.18	42.4	4.1
1.38	1.60	1.86	-14.0	11.5	1.38	1.81	1.18	53.4	4.3
CHLOROFORM					CHLOROFORM				
0.60	0.83	0.97	-14.4	17.3	0.60	0.98	0.54	81.5	6.8
0.78	0.99	1.11	-10.0	19.2	0.78	1.19	0.71	67.6	7.6
0.92	1.11	1.31	-15.3	20.4	0.92	1.34	0.77	74.0	8.2
1.10	1.25	1.38	-9.4	21.9	1.10	1.53	0.87	75.9	8.8
1.24	1.35	1.65	-18.2	22.9	1.24	1.66	0.99	67.7	9.3
1.38	1.44	1.76	-18.2	23.9	1.38	1.80	0.99	81.8	9.8

TABLE 59. COMPARISON OF MEASURED AND PREDICTED $K_\ell a$ (CONSTANT GAS LOADING) (CONCLUDED)

2-Inch Tri-Packs (G_v = 32.9 m•min^{-1})					Flexipac (G_v = 32.9 m•min^{-1})				
L_v (m•min^{-1})	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g	L_v (m•min^{-1})	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g
METHYLENE CHLORIDE					METHYLENE CHLORIDE				
0.60	0.83	1.07	-22.4	23.2	0.60	1.02	0.61	67.2	9.5
0.78	0.99	1.18	-16.1	25.5	0.78	1.24	0.75	65.3	10.6
0.92	1.09	1.37	-20.4	27.0	0.92	1.39	0.79	75.9	11.4
1.10	1.22	1.47	-17.0	28.8	1.10	1.58	0.85	85.9	12.3
1.24	1.31	1.76	-25.6	30.0	1.24	1.72	0.95	81.1	12.9
1.38	1.40	1.87	-25.1	31.1	1.38	1.85	0.88	110.2	13.5

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$)

G_v ($m \cdot min^{-1}$)	5/8-Inch Pall Rings Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	1-Inch Pall Rings Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
	TETRACHLOROETHYLENE					TETRACHLOROETHYLENE			
4.56	1.34	1.33	0.8	6.2	4.56	1.14	1.08	5.6	8.4
7.30	1.36	1.43	-4.9	4.5	18.25	1.21	1.25	-3.2	3.3
10.95	1.38	1.43	-3.5	3.4	25.55	1.21	1.21	0.0	2.7
16.43	1.39	1.49	-6.7	2.6	41.06	1.22	1.35	-9.6	1.9
25.55	1.40	1.41	-0.7	1.9					
32.85	1.41	1.42	-0.7	1.6					
36.50	1.41	1.52	-7.2	1.5					
	1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE			
4.56	1.38	1.43	-3.5	6.2	4.56	1.18	1.14	3.5	8.4
7.30	1.40	1.47	-4.8	4.6	18.25	1.24	1.38	-10.1	3.4
10.95	1.42	1.49	-4.7	3.5	25.55	1.25	1.37	-8.8	2.7
16.43	1.43	1.62	-11.7	2.6	41.06	1.26	1.54	-18.2	1.9
25.55	1.44	1.56	-7.7	2.0					
32.85	1.45	1.56	-7.1	1.6					
36.50	1.45	1.60	-9.4	1.5					

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_\ell a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

5/8-Inch Pall Rings					1-Inch Pall Rings				
G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
4.56	1.35	1.28	5.5	10.0	4.56	1.14	0.84	35.7	13.3
7.30	1.39	1.35	3.0	7.4	18.25	1.24	1.29	-3.9	5.5
10.95	1.42	1.36	4.4	5.7	25.55	1.25	1.32	-5.3	4.4
16.43	1.44	1.58	-8.9	4.3	41.06	1.27	1.46	-13.0	3.2
25.55	1.45	1.49	-2.7	3.2					
32.85	1.46	1.53	-4.6	2.7					
36.50	1.46	1.61	-9.3	2.5					
CHLOROFORM					CHLOROFORM				
7.30	1.32	1.09	21.1	16.2	18.25	1.21	1.08	12.0	12.3
10.95	1.38	1.27	8.7	12.7	25.55	1.24	1.21	2.5	10.0
16.43	1.42	1.44	-1.4	9.9	41.06	1.28	1.25	2.4	7.4
25.55	1.46	1.36	7.4	7.4					
32.85	1.48	1.38	7.2	6.3					
36.50	1.48	1.51	-2.0	5.9					

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
	5/8-Inch Pall Rings					1-Inch Pall Rings			
	METHYLENE CHLORIDE					METHYLENE CHLORIDE			
10.95	1.40	1.29	8.5	17.3	18.25	1.23	1.01	21.8	16.9
16.43	1.47	1.43	2.8	13.6	25.55	1.28	1.19	7.6	13.8
25.55	1.52	1.53	-0.7	10.4	41.06	1.33	1.50	-11.3	10.3
32.85	1.55	1.62	-4.3	8.9					
36.50	1.56	1.73	-9.8	8.3					
	2-Inch Pall Rings					1-Inch Flexisaddles			
	TETRACHLOROETHYLENE					TETRACHLOROETHYLENE			
4.56	0.90	1.00	-10.0	13.4	7.30	1.17	1.00	17.0	6.2
7.30	0.93	1.12	-17.0	10.1	14.60	1.20	1.12	7.1	3.9
14.60	0.97	1.17	-17.1	6.4	18.25	1.21	1.17	3.4	3.3
27.38	0.99	1.15	-13.9	4.2	25.55	1.21	1.15	5.2	2.7
50.19	1.01	1.22	-17.2	2.8	41.06	1.22	1.22	0.0	1.9

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_\ell a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

2-Inch Pall Rings					1-Inch Flexisaddles				
G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g
1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE				
4.56	0.92	1.04	-11.5	13.6	7.30	1.20	1.04	15.4	6.2
7.30	0.96	1.16	-17.2	10.1	14.60	1.23	1.16	6.0	3.9
14.60	1.00	1.21	-17.4	6.5	18.25	1.24	1.21	2.5	3.4
27.38	1.02	1.23	-17.9	4.3	25.55	1.25	1.23	1.6	2.7
50.19	1.03	1.24	-16.9	2.8	41.06	1.26	1.24	1.6	1.9
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
4.56	0.86	0.88	-2.3	20.7	7.30	1.18	0.88	34.1	10.0
7.30	0.92	1.05	-12.4	15.8	14.60	1.23	1.05	17.1	6.4
14.60	0.98	1.17	-16.2	10.4	18.25	1.24	1.17	6.0	5.5
27.38	1.01	1.23	-17.9	6.9	25.55	1.25	1.23	1.6	4.4
50.19	1.04	1.27	-18.1	4.7	41.06	1.27	1.27	0.0	3.2

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

2-Inch Pall Rings					1-Inch Flexisaddles				
G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
	CHLOROFORM					CHLOROFORM			
7.30	0.79	0.78	1.3	31.2	7.30	1.09	0.61	78.7	21.1
14.60	0.89	1.00	-11.0	21.9	14.60	1.18	0.78	51.3	14.1
27.38	0.97	1.09	-11.0	15.3	18.25	1.21	1.00	21.0	12.3
50.19	1.02	1.15	-11.3	10.5	25.55	1.24	1.09	13.8	10.0
					41.06	1.28	1.15	11.3	7.4
	METHYLENE CHLORIDE					METHYLENE CHLORIDE			
14.60	0.88	0.97	-9.3	28.8	14.60	1.20	0.59	103.4	19.2
27.38	0.98	1.14	-14.0	20.6	18.25	1.23	0.97	26.8	16.9
50.19	1.05	1.26	-16.7	14.5	25.55	1.28	1.14	12.3	13.8
					41.06	1.33	1.26	5.6	10.3

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

2-Inch Tri-Packs					Flexipac				
G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
TETRACHLOROETHYLENE					TETRACHLOROETHYLENE				
4.56	1.01	1.27	-20.5	20.1	4.56	1.22	0.70	74.3	8.0
7.30	1.07	1.29	-17.1	15.3	7.30	1.24	0.83	49.4	5.9
14.60	1.14	1.36	-16.2	10.0	14.60	1.27	0.90	41.1	3.7
32.85	1.19	1.35	-11.9	5.9	32.85	1.29	0.87	48.3	2.1
54.75	1.21	1.35	-10.4	4.2	54.75	1.30	0.96	35.4	1.5
1,1,1-TRICHLOROETHANE					1,1,1-TRICHLOROETHANE				
4.56	1.04	1.30	-20.0	20.3	4.56	1.25	0.74	68.9	8.1
7.30	1.10	1.32	-16.7	15.4	7.30	1.28	0.89	43.8	6.0
14.60	1.17	1.37	-14.6	10.1	14.60	1.31	0.94	39.4	3.8
32.85	1.22	1.37	-10.9	6.0	32.85	1.33	0.89	49.4	2.2
54.75	1.24	1.39	-10.8	4.3	54.75	1.34	0.99	35.4	1.5

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_{\ell}a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONTINUED)

2-Inch Tri-Packs					Flexipac				
G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_{\ell}a$ (min^{-1})	Meas. $K_{\ell}a$ (min^{-1})	% Diff.	% R_g
TRICHLOROETHYLENE					TRICHLOROETHYLENE				
4.56	0.93	1.20	-22.5	29.8	4.56	1.21	0.62	95.2	12.8
7.30	1.02	1.25	-18.4	23.4	7.30	1.26	0.79	59.5	9.6
14.60	1.12	1.34	-16.4	15.8	14.60	1.31	0.88	48.9	6.1
32.85	1.20	1.36	-11.8	9.6	32.85	1.34	0.87	54.0	3.6
54.75	1.24	1.37	-9.5	6.9	54.75	1.36	0.99	37.4	2.5
CHLOROFORM					CHLOROFORM				
4.56	0.69	1.07	-35.5	50.6	4.56	1.08	0.32	237.5	26.2
7.30	0.80	1.14	-29.8	42.4	7.30	1.16	0.51	127.5	20.4
14.60	0.96	1.23	-22.0	31.2	14.60	1.26	0.75	68.0	13.6
32.85	1.11	1.31	-15.3	20.4	32.85	1.34	0.77	74.0	8.2
54.75	1.18	1.28	-7.8	15.2	54.75	1.38	0.96	43.7	5.9

TABLE 60. COMPARISON OF MEASURED AND PREDICTED $K_\ell a$ (CONSTANT LIQUID LOADING L_v = 0.92 $m \cdot min^{-1}$) (CONCLUDED)

2-Inch Tri-Packs					Flexipac				
G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g	G_v ($m \cdot min^{-1}$)	Onda $K_\ell a$ (min^{-1})	Meas. $K_\ell a$ (min^{-1})	% Diff.	% R_g
METHYLENE CHLORIDE					METHYLENE CHLORIDE				
4.56	0.61	0.88	-30.7	59.6	4.56	1.04	0.17	511.8	33.9
7.30	0.73	0.97	-24.7	51.5	7.30	1.15	0.35	228.6	27.0
14.60	0.91	1.27	-28.3	39.5	14.60	1.28	0.69	85.5	18.5
32.85	1.09	1.37	-20.4	27.0	32.85	1.39	0.79	75.9	11.4
54.75	1.19	1.46	-18.5	20.6	54.75	1.44	1.03	39.8	8.3

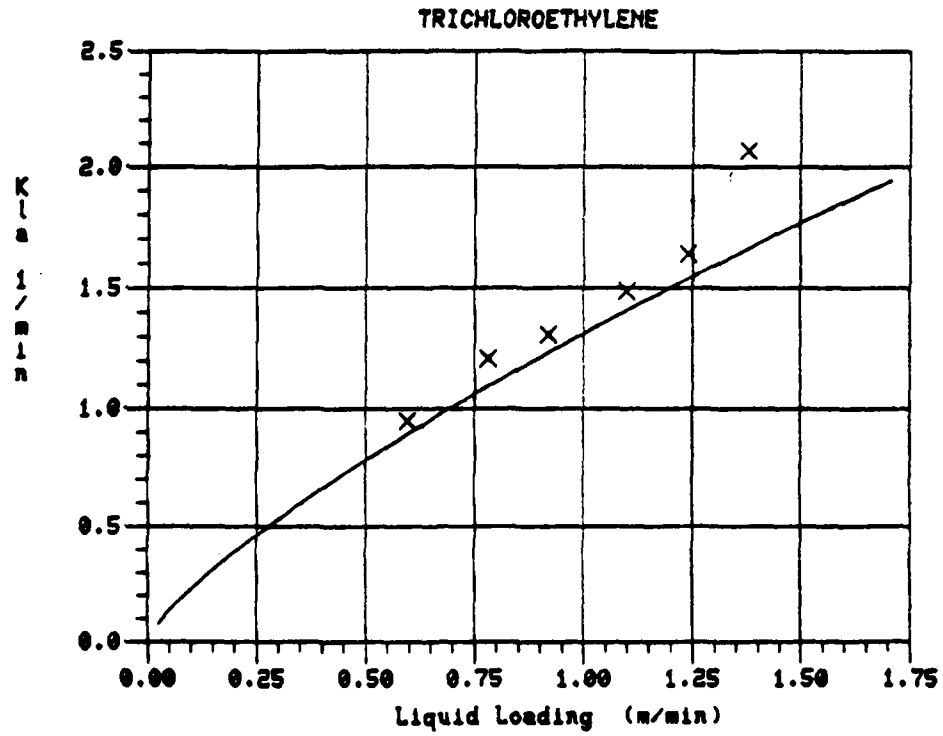

Figure 39. Effect of Liquid Loading on $K_\ell a$ for TCE (1-Inch Pall Rings, G_v = 25.6 m·min^{-1}, T = 25°C). Curve is Onda Correlation Prediction.

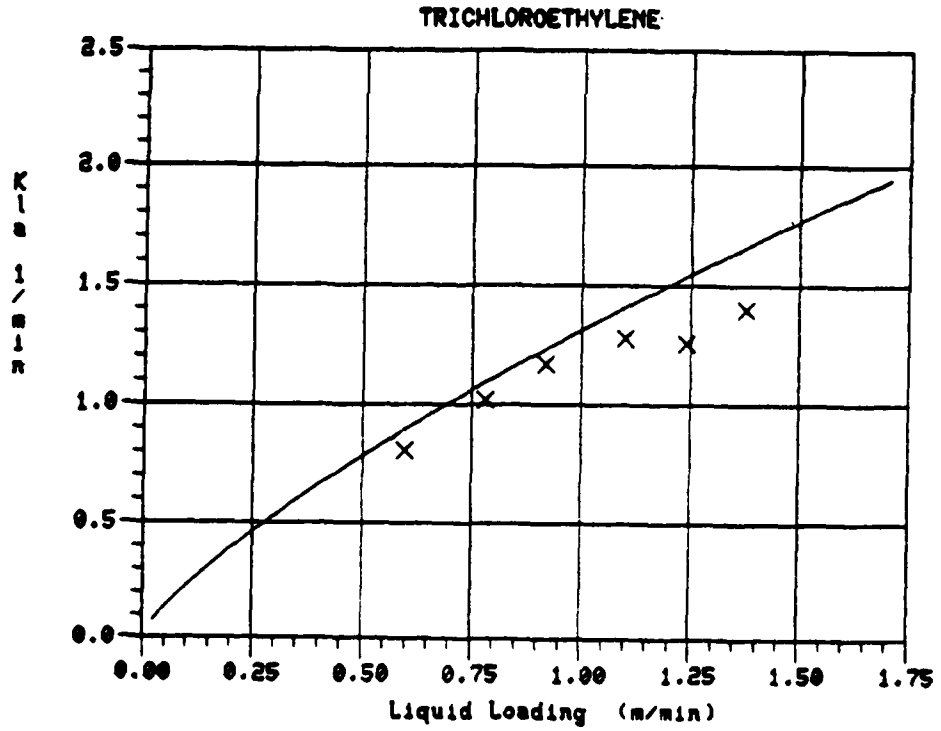

Figure 40. Effect of Liquid Loading on $K_\ell a$ for TCE (1-Inch Flexi-saddles, G_v = 25.6 m·min^{-1}, T = 25°C). Curve is Onda Correlation Prediction.

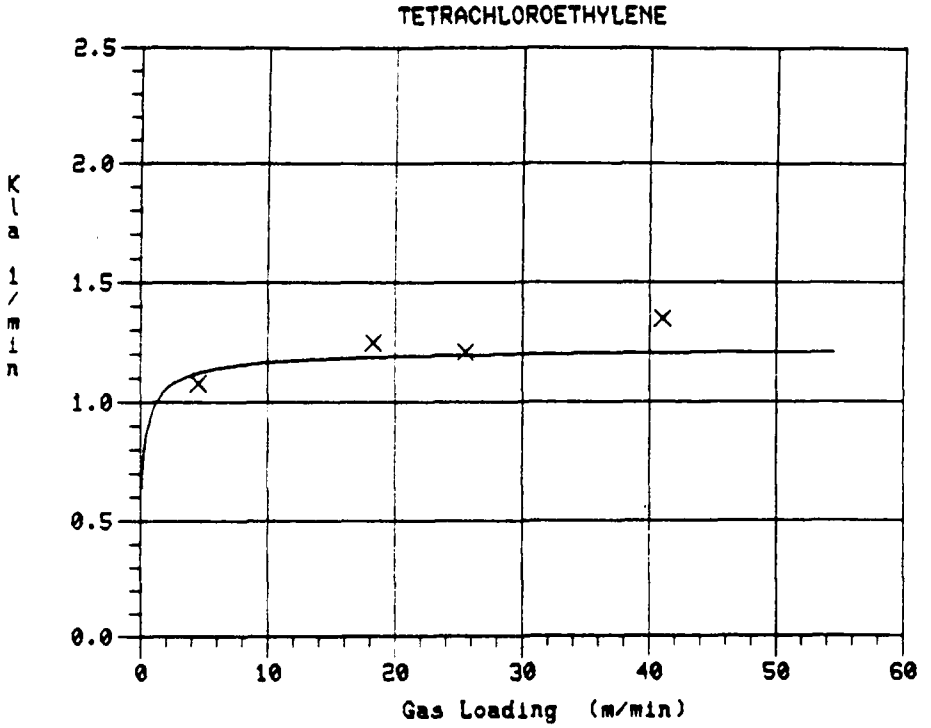

Figure 41. Effect of Gas Loading on $K_\ell a$ for Tetrachloroethylene (1-Inch Pall Rings, L_V = 0.92 m·min^{-1}, T = 25°C). Curve is Onda Correlation Prediction.

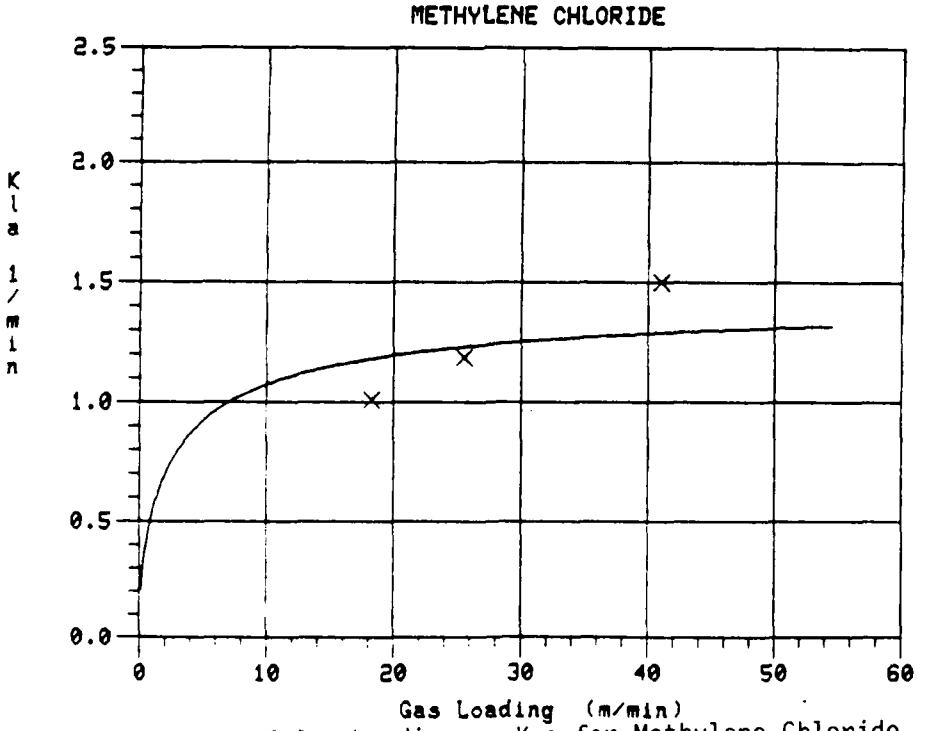

Figure 42. Effect of Gas Loading on $K_\ell a$ for Methylene Chloride (1-Inch Pall Rings, L_V = 0.92 m·min^{-1}, T = 25°C). Curve is Onda Correlation Prediction.

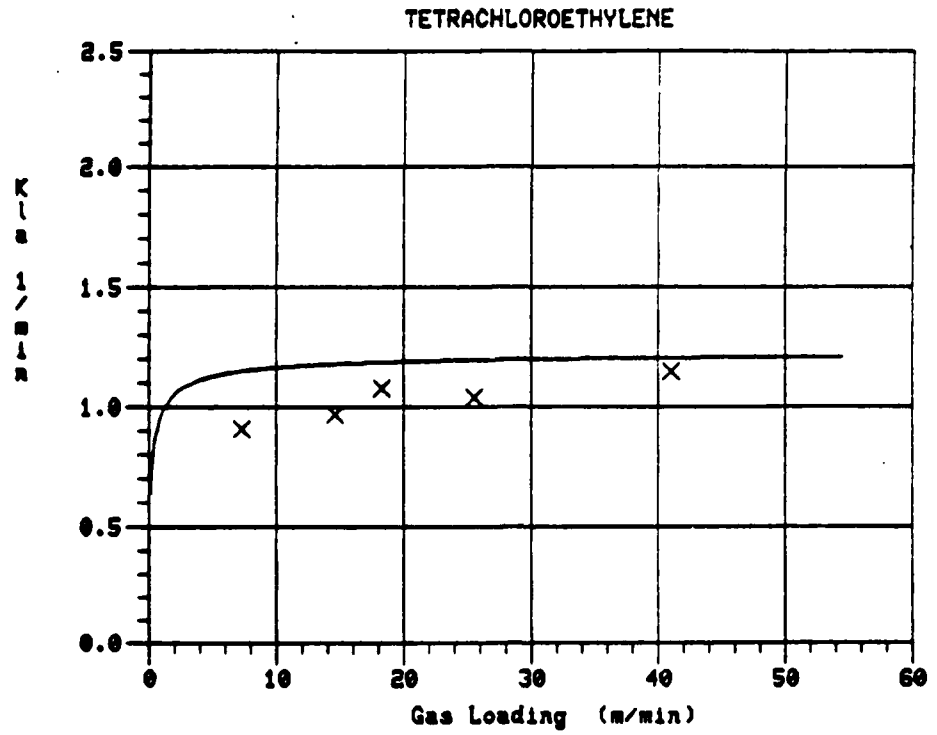

Figure 43. Effect of Gas Loading on $K_\ell a$ for Tetrachloroethylene (1-Inch Flexisaddles, L_V = 0.92 $m \cdot min^{-1}$, T = 25°C) Curve is Onda Correlation Prediction.

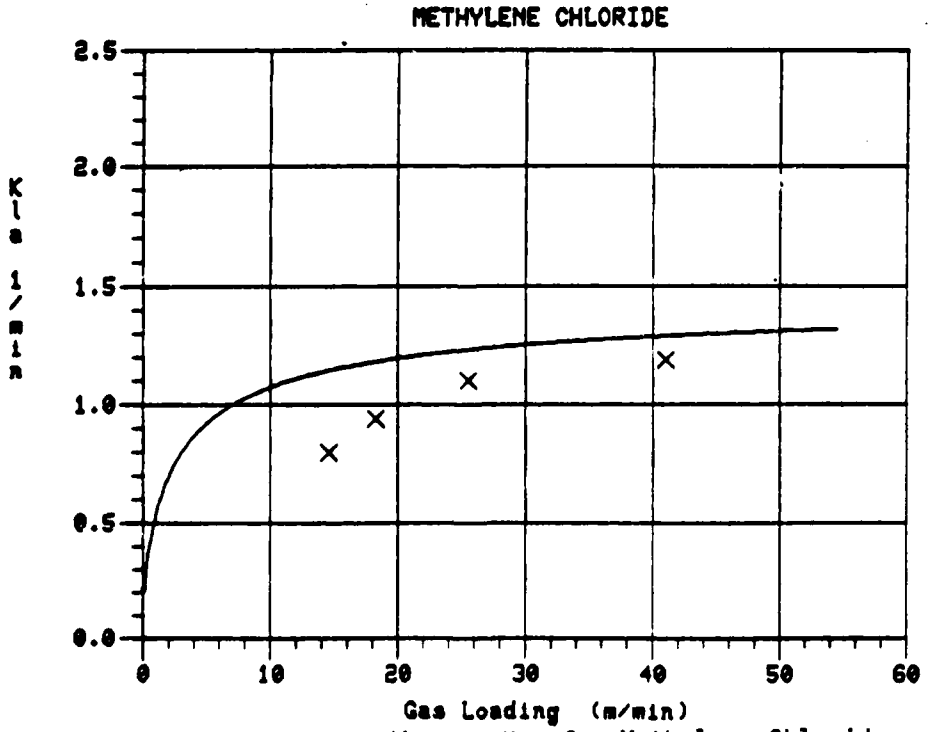

Figure 44. Effect of Gas Loading on $K_\ell a$ for Methylene Chloride (1-Inch Flexisaddles, L_V = 0.92 $m \cdot min^{-1}$, T = 25°C) Curve is Onda Correlation Prediction.

appreciable % R_g (i.e., low H_c, low G_v). Note that the data in Figures 42 and 44 show much greater dependence of $K_\ell a$ upon G_v than do the Onda curves.

A summary of measured and predicted $K_\ell a$'s for all runs made with Pall rings -- and for all compounds studied -- is shown in Figure 45. The solid line in the figure represents perfect agreement between predicted and measured $K_\ell a$'s; the dashed lines represent $\pm$ 20 percent deviations of predicted values from those observed. It appears that the Onda correlations are generally capable of fitting the Pall ring data to within $\pm$ 20 percent, which is about the accuracy claimed by Onda for his k_ℓ correlation. Note, however that there appear to be more data points below the line than above it, implying some systematic error in using the correlations with Pall rings, though perhaps slight.

A similar plot for 1-inch Flexisaddles and 2-inch Tri-Packs is shown in Figure 46. (Flexipac data are not shown -- and will not be discussed further -- due to the poor fit of this structured packing to our column, and the obvious, resulting flow distribution problems.) Note that, in general, Onda seems to overestimate $K_\ell a$ for 1-inch Flexisaddles, but has a tendency to underestimate values for the 2-inch Tri-Packs. The dotted lines in the figure have to become $\pm$ 30 percent lines in order to include most all data points.

Earlier analysis of data obtained over a range of temperatures (Figure 32) indicated inaccuracy, particularly in the Onda k_g correlation, resulting in greater errors as % R_g increases. A crude attempt to modify the combined Onda expressions for $k_\ell a$ and $k_g a$ via multiplication of each by constants λ and ϕ, respectively, was successful (Figures 33 and 34). However, it was earlier noted that, to be valid, the correction fators λ and ϕ would have to be found to remain constant for all packings. If not, then more complex modifications would be indicated.

Plots of % D (i.e., percent difference between Onda-predicted and observed $K_\ell a$ values) versus % R_g (i.e, percent gas-phase resistance as predicted by Onda correlations) are shown in Figures 47 through 51 for each of the packings, except 1-1/2-inch Pall rings and the Flexipac. (The former was not extensively studied; the latter was

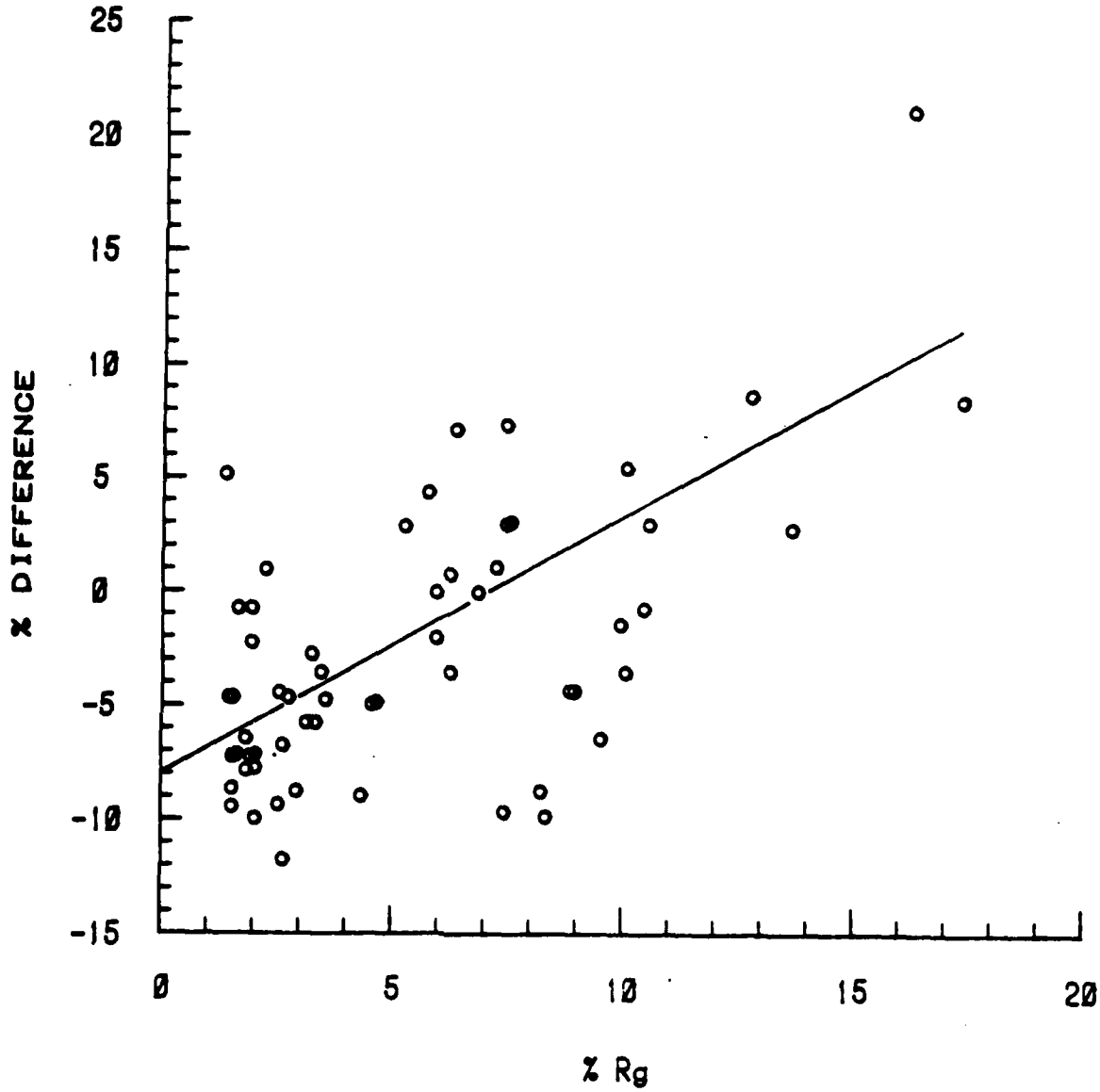

Figure 47. Percent Difference Between Onda-Predicted and Measured $K_\ell a$ Values vs % R_g (5/8-Inch Pall Rings, T = 25°C). Line Yields λ = 1.09, ϕ = 0.49.

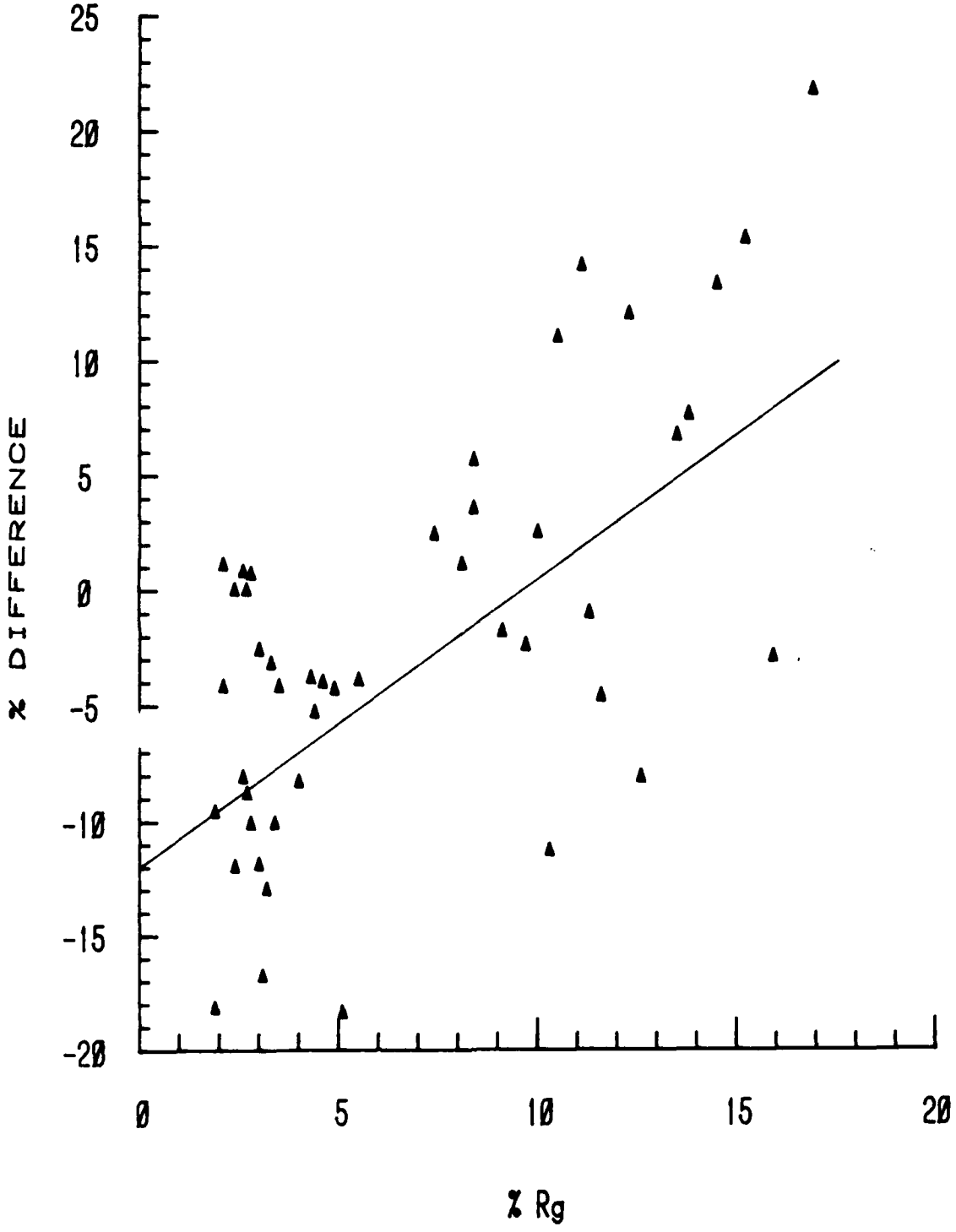

Figure 48. Percent Difference Between Onda-Predicted and Measured $K_\ell a$ Values vs % R_g (1-Inch Pall Rings, T = 25°C). Line Yields λ = 1.14, ϕ = 0.47.

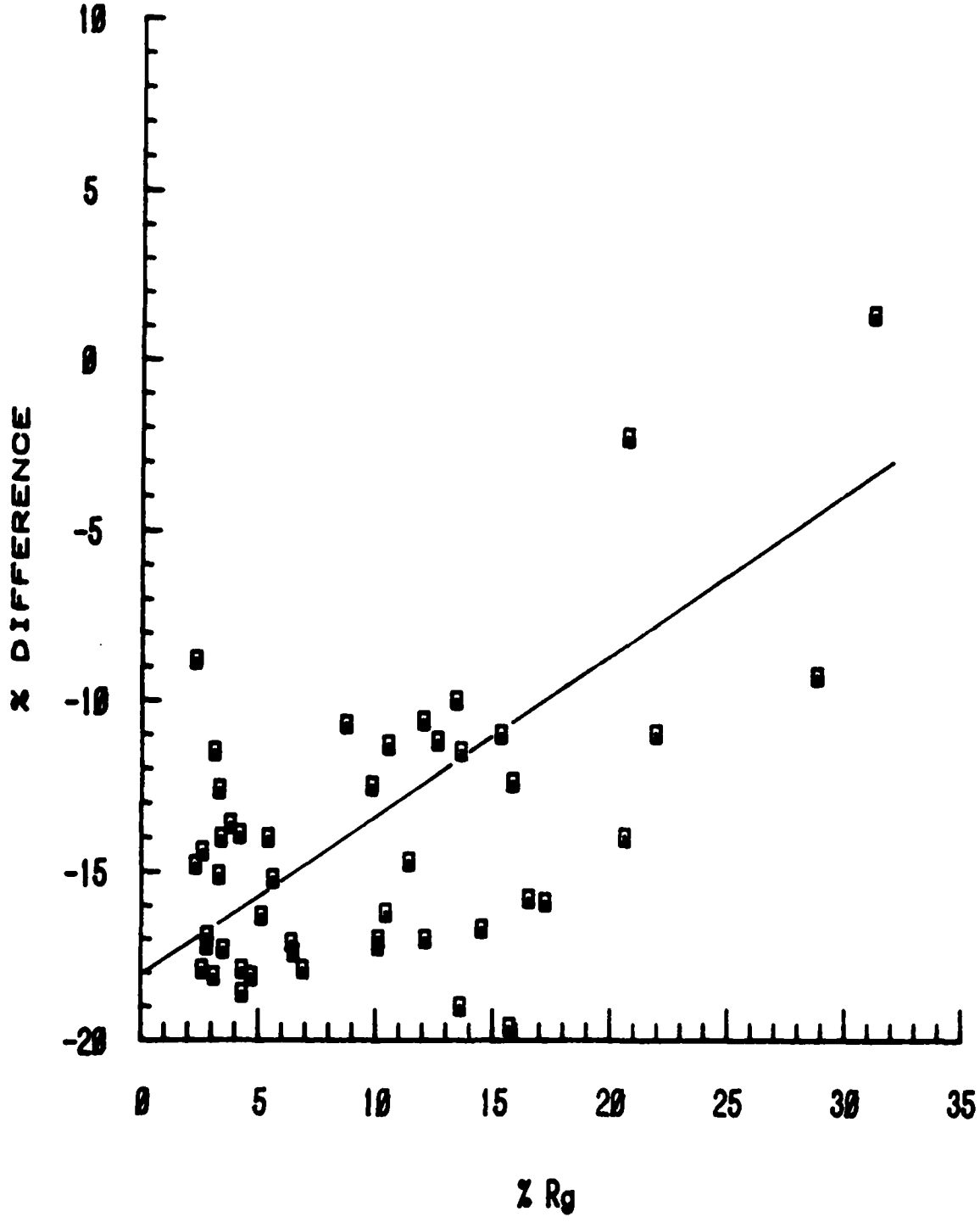

Figure 49. Percent Difference Between Onda-Predicted and Measured $K_\ell a$ Values vs % R_g (2-Inch Pall Rings, T = 25°C). Line Yields $\lambda = 1.22$, $\phi = 0.78$.

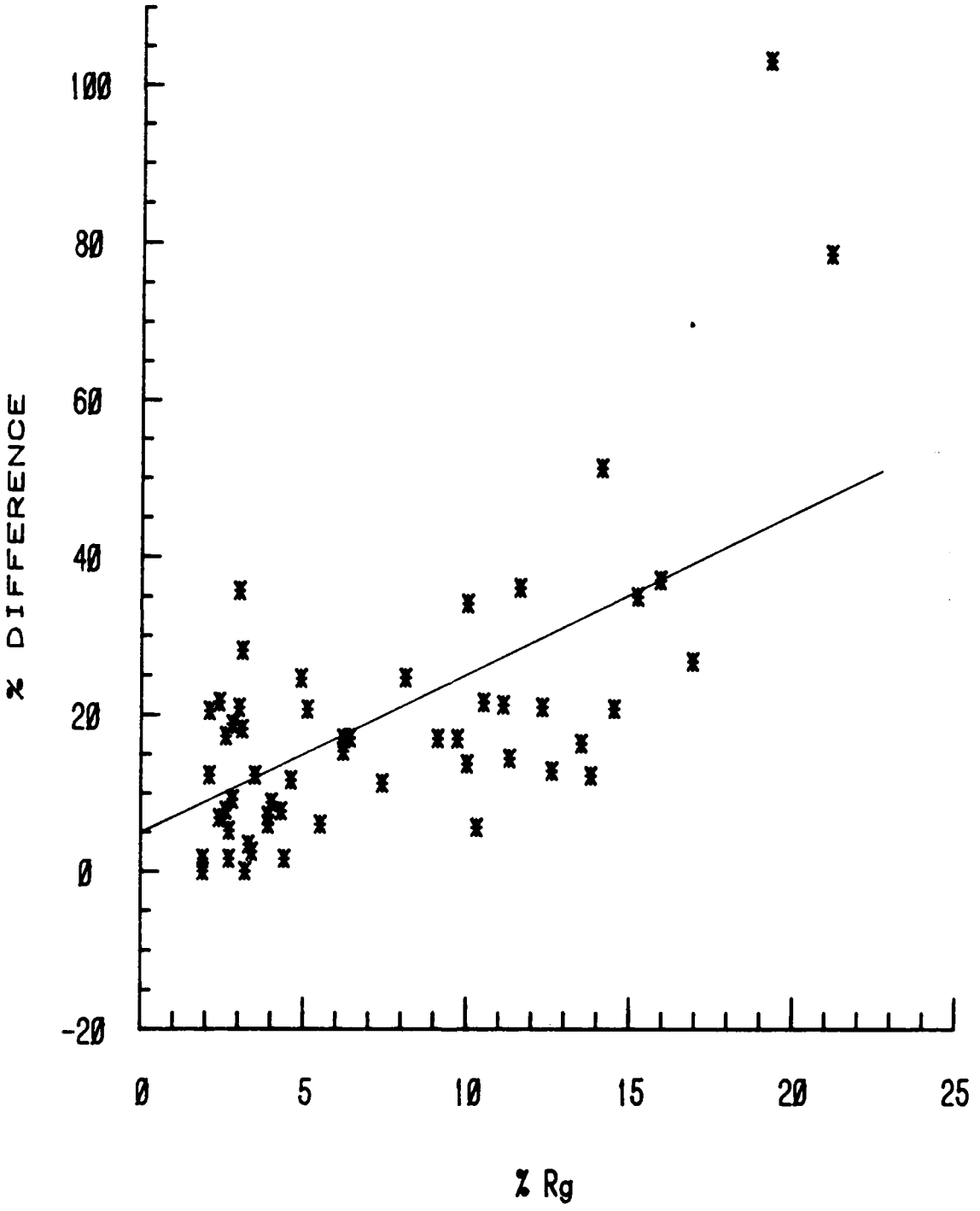

Figure 50. Percent Difference Between Onda-Predicted and Measured $K_\ell a$ Values vs % R_g (1-Inch Flexisaddles, T = 25°C). Line Yields λ = 0.95, ϕ = 0.33.

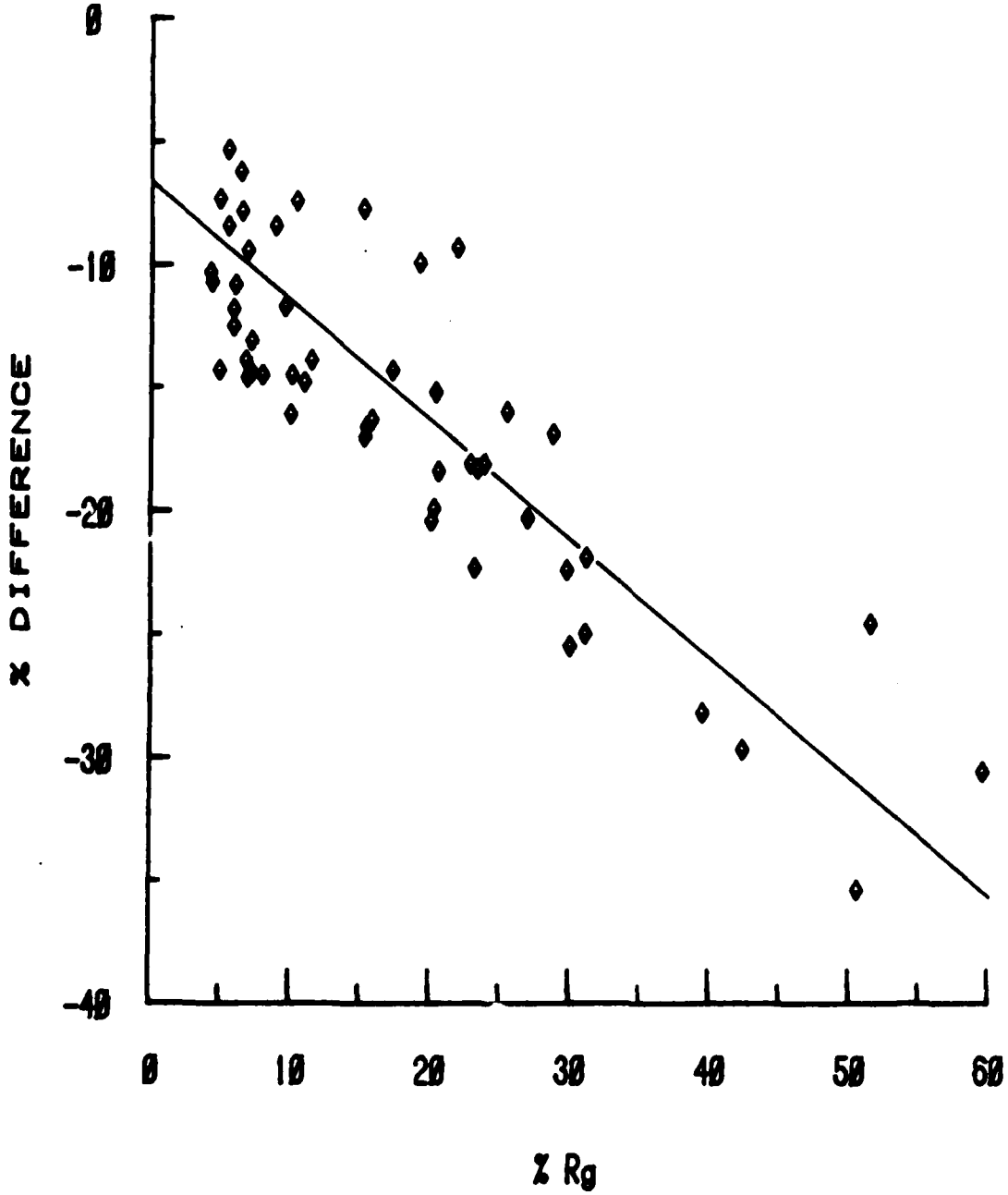

Figure 51. Percent Difference Between Onda-Predicted and Measured $K_\ell a$ Values vs % R_g (2-Inch Tri-Packs, T = 25°C). Line Yields $\lambda = 1.08$, $\phi = 2.22$.

a flawed sample.) Each figure contains data from all compounds studied. In accordance with Equation (111), λ and ϕ values were calculated for each and are summarized in Table 61. The lack of agreement among packings is noteworthy. All except Flexisaddles apparently require an increase in $k_\ell a$ estimates -- but by greatly differing factors. Flexisaddles, in fact, require a modest decrease in $k_\ell a$. All except Tri-Packs require decreased $k_g a$ estimates, again by radically different factors. Tri-Packs require $k_g a$ to be more than doubled! What's more, the same packing (1-inch rings) gave quite different results between the separate studies conducted with it. The difference experimentally was that % R_g was varied in the isothermal runs solely by variation in L_v, G_v, and solute; in the temperature studies, % R_g was varied solely by changing temperature and solute.

Considering all of the above findings, the implication is that -- while there may be possible improvement in the Onda predictions via alteration of frontal constants in the k_ℓ and k_g correlations -- there is certainly much else that is resulting in predictive error. For example, certainly there is no way that the Onda correlations, in their present form, can account for performance differences between 1-inch rings and 1-inch saddles, since the packing-specific parameters input to the correlations (i.e., d_p and a_t) are identical for rings and saddles. Additional packing-specific parameters need to be factored into the correlations, probably in the a_w expression, to account for the effects of packing geometry. Only in this manner can performance differences between rings and saddles be predicted quantitatively.

As McCabe and Smith (1976) point out: "In spite of much careful experimental work on coefficients...the characteristic particle size for packings of different shapes has not been chosen, and the effects of geometrical shape factors are unknown."

TABLE 61. APPROXIMATE CORRECTION FACTORS, λ and ϕ, NEEDED FOR ONDA-PREDICTED $k_\ell a$ AND $k_g a$ VALUES, RESPECTIVELY.

Packings	λ	ϕ
5/8-inch Pall Rings	1.09	0.49
1-inch Pall Rings (25°C)	1.14	0.47
1-inch Pall Rings (10°C-30°C)[a]	1.85	0.14
2-inch Pall Rings	1.22	0.78
1-inch Flexisaddles	0.95	0.33
2-inch Tri-Packs	1.08	2.22

[a]From Figure 32.

SECTION VII

SUMMARY AND CONCLUSIONS

A. EQUILIBRIUM STUDIES

An innovative method for measuring Henry's constants of volatile solutes in dilute aqueous systems was proposed and evaluated, termed Equilibrium Partitioning in Closed Systems (EPICS). This method relies upon measurement of the ratio of headspace concentrations from two equilibrated bottles containing equal solute masses, but possessing differing liquid volumes. Knowledge of the actual mass added to the two bottles is not required, nor is knowledge of the actual, resultant headspace concentrations; raw, surrogate measures such as gas-chromatographic peak heights suffice, so long as they are linearly related to actual concentration. The EPICS procedure is sensitive and useful for solutes with dimensionless Henry's constants less than about one. Precision averages about 5 percent.

Comparison of the EPICS procedure with a commonly used batch, diffused aeration method for measuring Henry's constant demonstrates that the EPICS procedure is at least as accurate, being free of mass transfer limitations which may affect the accuracy of other methods.

Henry's constant values were measured for five common volatile pollutants over the temperature range from 10° to 30°C. The five compounds employed were: tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, chloroform, and methylene chloride. Temperature regressions were calculated and are reported for each compound. Experiments employing mixtures of the five solutes demonstrate no mutual effects on Henry's constants at up to 375 mg/l total mixture concentration. Additionally, studies performed with the five solutes in the "mg/l" range, but in the presence of 200 mg/l phenol, showed no effect on Henry's constant. Using tetrachloroethylene, chloroform, and methylene chloride (in separate experimental studies), the effect of ionic strength on the activity coefficient of the aqueous solute was determined up to 1M KCl. "Salting-out" coefficients were thus derived. Significant (> 10 percent) increases in activity do not occur until the ionic strength of the system exceeds 0.26M (KCl).

B. DIFFUSIVITY STUDIES

Liquid-phase diffusivity values were measured for the five study compounds at 20°C using a diaphragm diffusion cell. Due to solute mass losses through septa, the data were somewhat imprecise. Therefore, comparison of values with diffusivities estimated via several, available correlations was inconclusive. Nothing in the results obtained here contraindicates the use of "popular" correlations such as those of Wilke and Chang.

C. PACKED-TOWER STUDIES

Packed-tower air-stripping studies were performed using a pilot-scale facility of 44.5 cm (17.5-inch) ID x 2.44-meter (8-foot) packed height. Seven polypropylene packings were evaluated: 5/8, 1, 1 1/2, and 2-inch Pall rings; 1-inch Flexisaddles; 2-inch Tri-Packs; and a structured packing (Flexipac). Temperatures were controlled and studied over the range from 10° to 30°C. Liquid loading ranged from 0.6-1.38 $m \cdot min^{-1}$; gas loading ranged from 4.6-50 $m \cdot min^{-1}$. The same five volatile compounds were studied in these experiments as were used in all other phases of this research effort.

Studies performed with mixtures of all five solutes in the "mg/l" range showed no effect on the $K_\ell a$ value of each caused by the mutual presence of the others. The additional presence of substantial amounts of methanol used to predissolve the solutes caused no discernible effect on the $K_\ell a$ of each.

The effect of temperature on $K_\ell a$ could be equally well-correlated through use of simple arithmetic ($K_\ell a$ vs. T), logarithmic ($\ln K_\ell a$ vs. T or $\ln K_\ell a$ vs. 1/T) or viscosity-based ($K_\ell a$ vs. $T^{1/2}\ \mu_\ell^{-4/3}$) expressions; however, due to the complexity of $K_\ell a$ dependence upon liquid and gas-phase parameters, these specific expressions are not expected to be applicable beyond the ranges of their derivation.

The Onda correlations for predicting $K_\ell a$ were evaluated in these studies. For all sizes of Pall rings, agreement with measured values was within 20 percent, considered as good as could be expected. However, for other packings the $K_\ell a$ correlations sometimes

considerably overestimated (i.e., 1-inch Flexisaddles), and sometimes underestimated (i.e., 2-inch Tri-Packs) values. $K_\ell a$ data from Flexisaddles and Tri-Packs could be generally fit within $\pm$ 30 percent by the Onda correlations. Considering that the precision in measured $K_\ell a$ values is in the neighborhood of $\pm$ 10 percent, this level of agreement may suffice for many design purposes, if accompanied by an appropriate factor of safety.

Analysis of the $K_\ell a$ data and their deviations from correlation predictions demonstrate that no simple alteration of predicted $k_\ell a$ or $k_g a$ values (i.e., liquid and gas-phase resistances) by constant factors can consistently improve predictive ability. Observed performance differences between 1-inch Pall rings and 1-inch Flexisaddles indicate that geometric parameters need to be incorporated into the correlations to properly modify them.

Pressure drop measurements across the packed bed indicate inconsistent agreement between observed values and estimations provided by generalized correlations or manufacturer-supplied pressure-drop curves. Problems of scale-down are supposed.

APPENDIX A

PERTINENT DATA FOR COMPOUNDS STUDIED

Most of the data listed below are from Perry and Chilton (1973). The additional solubility references are:

A) Dilling (1975)

B) EPA (1980).

The densities given are relative to water at 4°C.

CHLOROFORM

Chemical Formula	$CHCl_3$
Molecular Weight	119.39
Density	1.489 @ 20°C
Boiling Point	61.2°C
Solubility in Water (mg/l)	8200 @ 20°C
	7840 @ 25°C (B)
Vapor Pressure (mm Hg)	200 @ 25.9°C

o-DICHLOROBENZENE

Chemical Formula	$C_6H_4Cl_2$
Molecular Weight	147.01
Density	1.305 @ 20°C
Boiling Point	179°C
Solubility in Water (mg/l)	100 @ 25°C (B)
Vapor Pressure (mm Hg)	1 @ 20.0°C

METHYLENE CHLORIDE

Chemical Formula	CH_2CCl_2
Molecular Weight	84.94
Density	1.336 @ 20°C
Boiling Point	40.5°C
Solubility in Water (mg/l)	20,000 @ 20°C
	16,700 @ 25°C (B)
	19,400 @ 25°C (A)
Vapor Pressure (mm Hg)	400 @ 24.1°C

TETRACHLOROETHYLENE

Chemical Formula	C_2Cl_4
Molecular Weight	165.85
Density	1.624 @ 15°C
Boiling Point	120.8°C
Solubility in Water (mg/l)	200 @ 20°C
	150 @ 25°C (B)
	140 @ 25°C (A)
Vapor Pressure (mm Hg)	20 @ 26.3°C

1,1,1-TRICHLOROETHANE

Chemical Formula	CH_3CCl_3
Molecular Weight	133.42
Density	1.325 @ 26°C
Boiling Point	74.1°C
Solubility in Water (mg/l)	720 @ 20°C (A)
	4400 @ 25°C (B)
Vapor Pressure (mm Hg)	100 @ 20.0°C

TRICHLOROETHYLENE

Chemical Formula	$CHCl\ CCl_2$
Molecular Weight	131.40
Density	1.466 @ 15°C
Boiling Point	87.2°C
Solubility in Water (mg/l)	1100 @ 25°C (A)
	1000 @ 25°C
Vapor Pressure (mm Hg)	60 @ 20.0°C

AD-A158 811 MASS TRANSFER COEFFICIENTS AND HENRY'S CONSTANTS FOR PACKED-TOWER AIR STR.. (U) CORNELL UNIV ITHACA NY DEPT OF CIVIL ENGINEERING J M GOSSET ET AL. JUN 85 4/4

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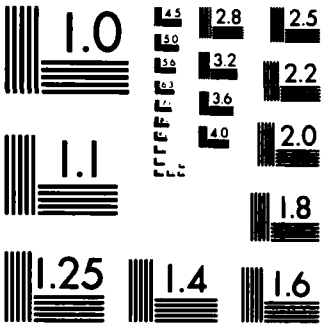

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APPENDIX B

ESTIMATING GAS-PHASE DIFFUSIVITIES

Solute diffusivity in the gas phase was estimated using the Hirschfelder correlation (Bird et al., 1960):

$$D_g = \frac{0.0018583 \sqrt{T^3 \left(\frac{1}{M_1} + \frac{1}{M_2}\right)}}{\left(P\ \sigma_{12}^2\ \Omega_{D,12}\right)10^4} \qquad \text{(B-1)}$$

where:

D_g = gas-phase solute diffusivity ($m^2 \cdot s^{-1}$);
T = absolute temperature (°K);
M_1 = molecular weight of solute;
M_2 = molecular weight of solvent gas (air, in this case: 28.97 g/mol);
P = absolute pressure (atm);
σ_{12} = Lennard-Jones characteristic collision diameter with respect to components 1 and 2 (A);
$\Omega_{D,12}$ = collision integral (dimensionless).

For nonpolar, nonreacting, molecule pairs, σ_{12} can be estimated by combining the Lennard-Jones parameters of species 1 and 2 empirically:

$$\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2) \qquad \text{(B-2)}$$

Values of σ_1 and σ_2 are tabulated in many sources (e.g., Hirschfelder et al., 1954) or may be estimated as:

$$\sigma = 1.18\ V_b^{1/3} \qquad \text{(B-3)}$$

where:

V_b = molar volume of the specie at its normal boiling point ($cm^3 \cdot mol^{-1}$).

The collision integral, $\Omega_{D,12}$, is a function of the dimensionless parameter $T\kappa/\epsilon_{12}$, where κ = Boltzmann constant = 1.38×10^{-6} erg °K^{-1}; and ϵ_{12} = energy of molecular interaction, in ergs:

$$\frac{\epsilon_{12}}{\kappa} = \left[\left(\frac{\epsilon_1}{\kappa}\right)\ \left(\frac{\epsilon_2}{\kappa}\right)\right]^{1/2} \qquad \text{(B-4)}$$

Values of ε_1 and ε_2 are tabulated in many sources (e.g., Hirschfelder et al., 1954), or may be estimated as:

$$\frac{\varepsilon}{\kappa} = 1.15\ T_b \qquad \text{(B-5)}$$

where:

T_b = normal boiling point (°K).

Once values of $T\kappa/\varepsilon_{12}$ are known, tables or correlations may be consulted which give $\Omega_{D,12}$ values as a function of $T\kappa/\varepsilon_{12}$. Table B-1 shows parameter values and resulting D_g values estimated for 1 atm, 298°K.

Over the temperature range of interest, the temperature variation of the $\Omega_{D,12}$ parameter, coupled with the $T^{3/2}$ dependence explicitly appearing in Equation (B-1), yields an approximate dependence of:

$$D_g^{T(°K)} = D_g^{298} \left(\frac{T(°K)}{298}\right)^{1.88} \qquad \text{(B-6)}$$

This equation was used to adjust D_g data to temperatures other than 25°C.

TABLE B-1. GAS-PHASE DIFFUSIVITY ESTIMATION (1 atm, 298°K).

Compound	M	σ(A)	ε/κ(°K)	$\kappa T/\varepsilon_{12}$	$\Omega_{D,12}$	σ_{12}(A)	D_g^{298} ($m^2 \cdot s^{-1}$)
Air	28.97	[a] 3.617	[a] 97	----	-----	-----	
MC	84.9	[a] 4.759	[a] 406	1.50	1.198	4.188	9.79×10^{-6}
Chl	119.4	[a] 5.430	[a] 327	1.67	1.148	4.524	8.43×10^{-6}
TCE	131.4	[b] 5.442	[b] 414	1.49	1.201	4.530	7.96×10^{-6}
1,1,1	133.4	[b] 5.576	[b] 399	1.51	1.195	4.597	7.75×10^{-6}
Tetra	165.9	[b] 5.755	[b] 453	1.42	1.226	4.686	7.15×10^{-6}

[a] From Bird et al. (1960).

[b] From Equation (B-3).

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